

Internal Correspondence

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T. E. MYRICK

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RAP86-39



ENVIRONMENTAL RESTORATION  
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T. E. Myrick, 3047, ORNL

### A Ranking of Contaminant Sources in the White Oak Creek Drainage

#### Scope

The purpose of this letter report is to present a ranking of contaminant sources in the White Oak Creek drainage. The basis of the ranking is a combination of results from a survey of the presence of water-borne contaminants in streams in the White Oak Creek drainage, obtained by Dr. T. Cerling, and data provided by K. Daniels, L. Melroy, and E. Davis from flow measurements in the basin. Presence of contaminants was assayed using streambed materials that were either suspended in the flow (active sources) or collected from the channel bottom (historical sources) during the July and August 1985, time period, then analyzed to determine the change in contaminant content. Flow data were compiled into volume totals for the July 1 - August 31 period, then converted to an average flow rate for that interval. The product of flow rate in cubic feet per second (cfs) and total accumulated contaminant in Bequerels per kilogram for nuclides or parts per million extractable metal for zinc was used as a relative indicator of flux. Since the level of detail for flow data was somewhat limited, the ranking has been confined to the level of waste management areas, as they are shown in Figure 1.

#### Contaminant Survey Results

The results of Dr. Cerling's stream surveys were presented in part in an earlier letter report (RAP86-20). The most recent progress report, which includes an update on major element chemistry and metal contamination in the White Oak Creek drainage basin, is attached to this report. Concentration data for this evaluation were taken from these two sources.

#### Flow Data for the White Oak Creek Drainage

The bulk of the flow data for the basin were made available from the files maintained by the Department of Environmental Management by K. Daniels. These data are taken from permanent flow monitoring structures that have been instrumented with flow totalizers. At most sites, the flow totalizers are read periodically to determine the volume of water that has passed the weir or flume between readings. There are no records of the instantaneous discharge readings that are processed. Previous studies have shown that records can contain systematic errors in excess of 20%, usually overestimating the flow. More recent work to improve operation and calibration of the equipment has generally improved the situation, especially at the confluence of White Oak Creek and Melton Branch, and at White Oak Dam. Data for SWSA are collected by staff from the Environmental Sciences Division, using continuous record charts. These data are processed to provide daily and

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T. E. Myrick  
Page 2  
April 28, 1986

monthly flow rates, as well as daily maximum and minimum instantaneous values. Data for SWSA 6 are collected using digital punched tape records of stage height, which is then converted to daily and monthly records similar to those for SWSA 4. All data were summarized for a common time base that includes the 62 days between July 1 and August 31, 1985 (midnight to midnight). It was assumed that the average flow rate between readings of the flow integrators could be used to estimate partial periods. A map showing sites of flow measuring stations is presented in Figure 2.

#### Product of Flow Rate and Concentration

Table 1 presents the combined flow, concentration, and product ( $Q \cdot C$ ) values. The product value has been assumed to be a relative indicator of flux, hence a reasonable basis for ranking present discharge of contaminants through the flow system. No importance should be assigned to the absolute magnitude of the product values beyond the first significant figure, and then only for purposes of relative ranking. Subsequent work, employing distribution coefficients, will explore possibilities for estimating actual fluxes from these data, but that is beyond the scope of this work. Table 2 shows a similar basis for ranking, using historical fluxes.

Results can be divided among four specific indicators of contamination:  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ , and zinc. The zinc is assumed to be an overall indicator of metal contamination, probably resulting from cooling tower operation. General rankings are:

<u><math>^{60}\text{Co}</math></u>	<u><math>^{90}\text{Sr}</math></u>	<u><math>^{137}\text{Cs}</math></u>	<u>Zinc</u>
HFIR/TRU WMA 8	PWTP	WMA 2	4500 Cooling Tower
PWTP WMA 2	1ST CR. WMA 2	PWTP WMA 2	HFIR/TRU WMA 8
	SWSA 5 WMA 5		
	SWSA 4 WMA 4		
	HRE WMA 9		
	5TH CR. WMA 2		

The above rankings represent a summary of the major sources that were active during the study period. The dominant result was the apparent importance of the Process Waste Treatment Plant (PWTP) to the release of radionuclides. It was the only significant active source of  $^{137}\text{Cs}$  in the basin, and the highest ranking  $^{90}\text{Sr}$  source. It also appeared to be the second most important source of  $^{60}\text{Co}$  in the basin. Recent improvements in the plant have reduced the magnitude of these inputs, but more recent data are not available to evaluate their effects. The HFIR/TRU area, which is waste management area (WMA) 8, was the major  $^{60}\text{Co}$  source in the basin. It also exhibited metal contamination, probably associated with cooling tower operation. The major  $^{90}\text{Sr}$  sources

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T. E. Myrick  
Page 3  
April 28, 1986

were more widely distributed than those for other contaminants. Although the flow had to be estimated by difference, which weakens the result, it appears that First Creek has become a significant  $^{90}\text{Sr}$  contributor at some point during the past 8 years. Earlier work by Cerling and Spalding did not show this source, but recent work has confirmed the ranking shown above. It appears the activity is entering First Creek from the main plant area to the east, through culvert pipes that discharge into First Creek. SWSA 5 appeared to be a slightly larger source of  $^{90}\text{Sr}$  during the survey than SWSA 4. This may be attributed to the time of year the survey was taken and perhaps to the 1983 water diversion that has reduced flow from the SWSA 4 tributary. The remaining two sources are the pond at the HRE site, which was buried and capped several years ago, and a point above monitoring station 2 on White Oak Creek. It has been surmised that the latter source is on Fifth Creek, based on information from limited studies there in March 1985.

Taking all data together, the ranking of waste management areas for remedial action studies based on active discharges would be WMA's 2, 8, 5, 4, and 9 as of last August. Other WMAs will require more detailed evaluation, and are likely to be of lower concern based on current releases. Dr. Cerling has pointed out that there is an increase in the discharge of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in the eastern portion of SWSA 6 tributaries. Although the low flows render this source as minor, the area does merit attention (WMA 6).

The results presented here are to be prepared in more final form in June, when Dr. Cerling submits his final report, but it is not likely the conclusions concerning relative rankings of major nuclide contaminants will change.



D. D. Huff, 1505, MS-002, ORNL (4-7859)

DDH:jsc

#### Attachments

cc: T. E. Cerling, University of Utah  
K. W. Cook  
N. H. Cutshall  
E. C. Davis  
L. D. Hyde  
J. T. Kitchings  
J. R. Lawson  
W. E. Manrod

C. B. Sherwood  
D. K. Solomon  
S. H. Stow  
L. E. Stratton  
J. R. Trabalka  
L. D. Voorhees  
File - DDH - NoRC

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**ORNL**  
**CENTRAL FILES NUMBER**

ORNL/CF-86/18

**DATE:** May 5, 1986

**SUBJECT:** Stable Isotope Analysis of Fracture-Filling Minerals in Shales and Limestones:  
Preliminary Scoping Studies and Assessment of the Applicability of the Technique

**TO:** Distribution

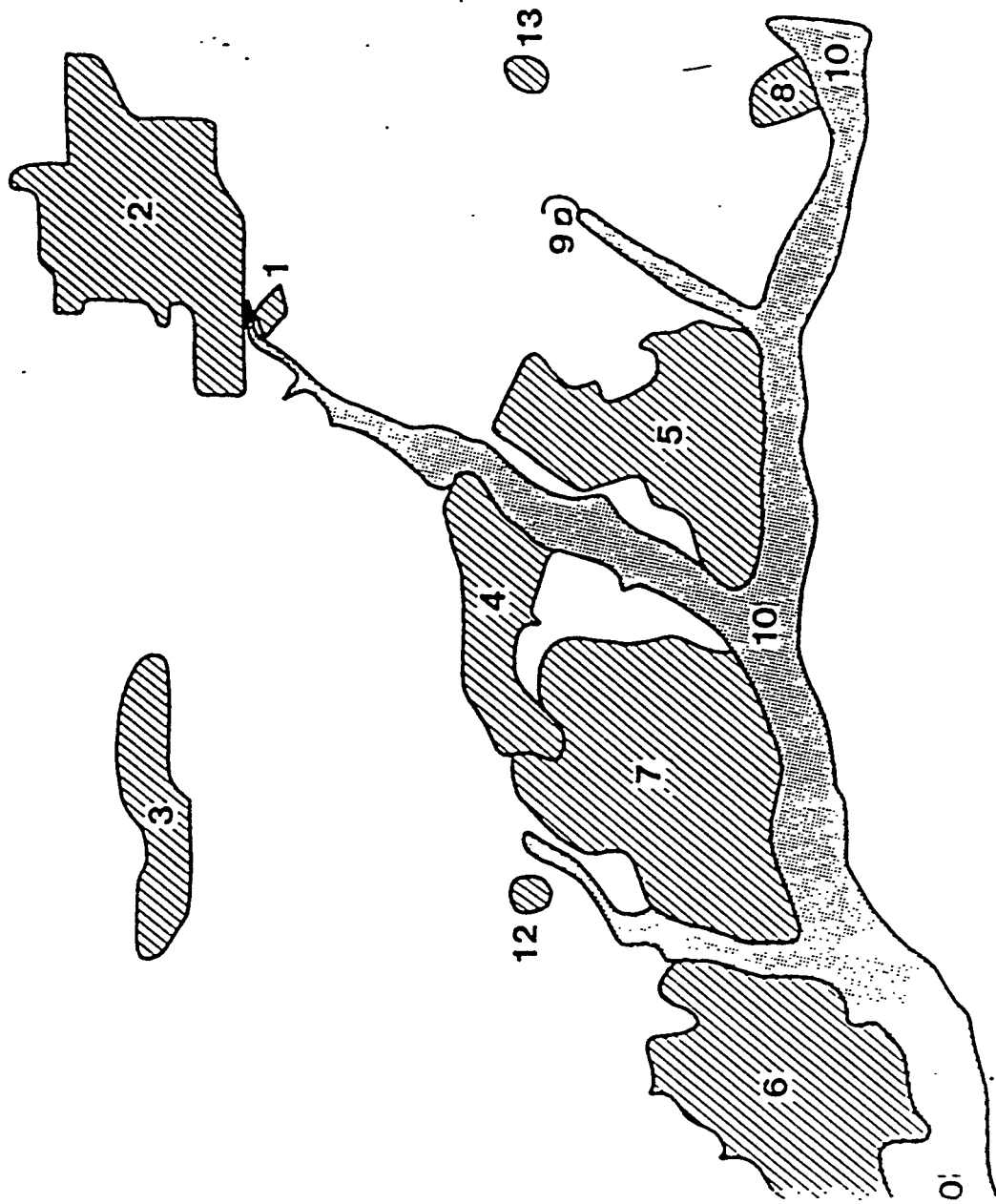
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D. M. Rye, Department of Geology and Geophysics,  
Yale University, New Haven, Connecticut

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| 19. A. D. Kelmers  | 41. ORNL Patent Office          |
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| 22. F. T. Lomenick |                                 |

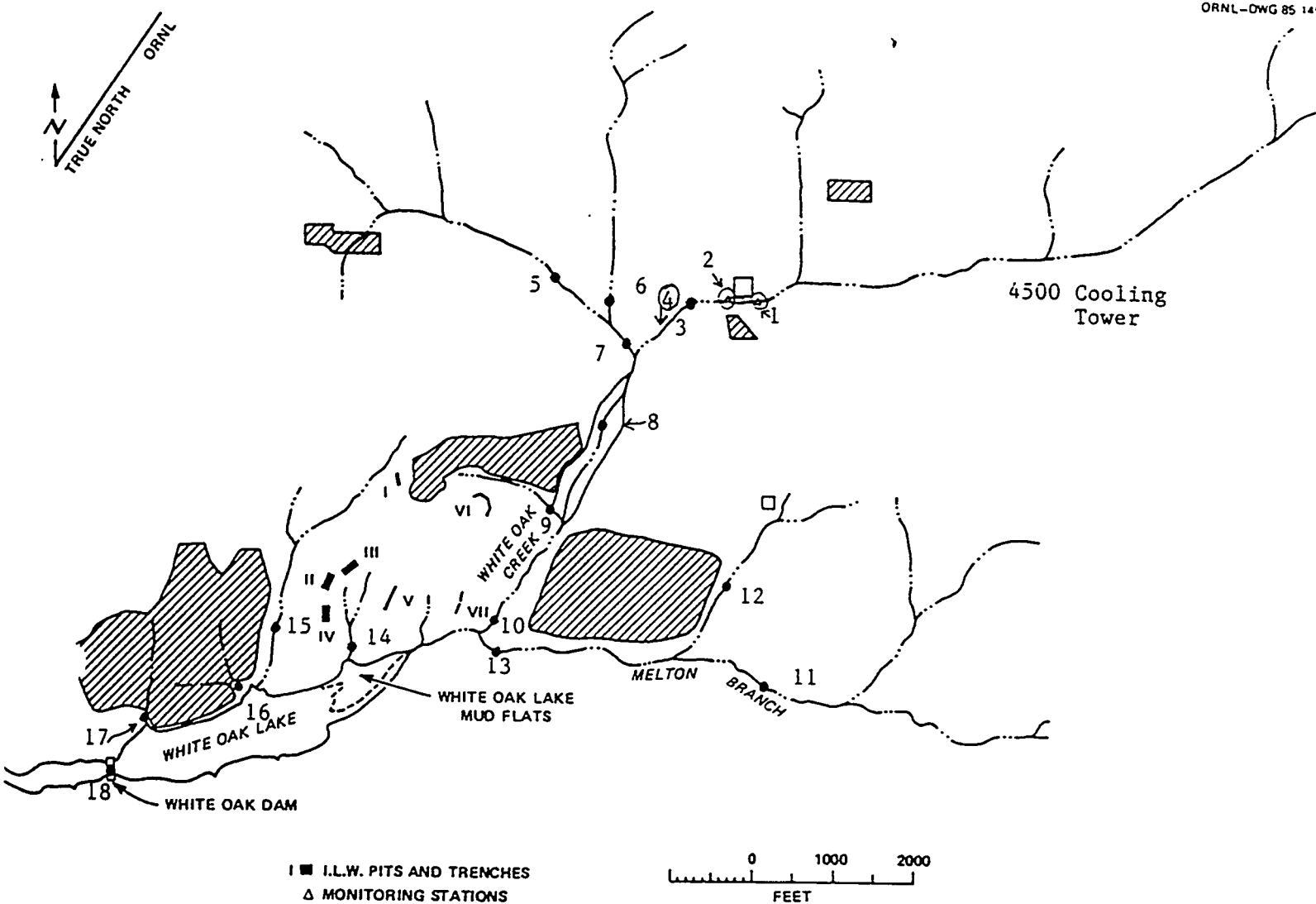
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- 1 SWSA 1
- 2 MAIN PLANT AREA
- 3 SWSA 3
- 4 SWSA 4
- 5 SWSA 5
- 6 SWSA 6
- 7 PITS AND TRENCHES
- 8 HFIR / TRU IMPOUNDMENTS
- 9 HRE CLOSED POND
- 10 WHITE OAK LAKE -
- WHITE OAK CREEK
- 11 GAS STATION
- 12 4-ACRE SITE
- 13 MELTON VALLEY LLW LEAK

WASTE MANAGEMENT AREAS AT ORNL  
(Scale: 1"=2,000')



STATION  
NUMBER

IDENTIFIER

1	MS-2 (Flume)
2	PWTP
3	3RD St.
4	STP
5	NWT
6	First Creek
7	MWT + First Creek
8	MS-2A (7500 Bridge)
9	T-2A (SWSA 4 Tributary)

STATION  
NUMBER

IDENTIFIER

10	MS-3
11	MS-4A
12	MS-4B (Melton Branch)
13	MS-4 (Melton Branch)
14	E. Seep
15	W. Seep
16	SWSA 6 (East)
17	SWSA 6 (West)
18	White Oak Dam

Figure 2. Stream Channels and Flow Measuring Sites  
in the White Oak Creek Drainage

Table 1. Indicator Calculations of White Oak Creek Active Fluxes

MAP No.	SITE	JUL-AUG VOLUME (MG)	AVG FLOW (CFS)	60Co		90Sr		137Cs		Zn	
				CONC	Q*C	CONC	Q*C	CONC	Q*C	CONC	Q*C
1	MS-2	351.3	8.78	5	43	23	202	10	87	150	1317
2	PWTP	12.4	0.31								
3	3RD ST	363.7	9.09	160	1454	220	2000	26000	236405	150	1363
4	STP	15.6	0.39								
5	NWT	7.0	0.18	5.0	0	510	89	49	8	105	18
6	FIRST CR. <sup>a</sup>		2.50								
7	NWT+1ST CR		2.68	5.0	13	510	1366	49	131	105	281
SUBTOTAL		386.3	12.16		1468		3367				1645
8	MS-2A	526.5	13.16	150.0	1974	340	4475	11000	144787		
9	T-2A(BG4)	2.1	0.05	5	0	9800	514	54	2	10	0
SUBTOTAL		528.6	13.22								
10	MS-3	502	12.55	110	1380	350	4392	7700	96635	71	891
11	MS-4A	72.1	1.80	4000	7210	10	18	26	46	220	396
12	MS-4B	9.3	0.23	3	0	980	227	290	67	19	4
SUBTOTAL		81.4	2.03		7210						
13	MS-4	109	2.73	355	967	410	1117	25	68	90	245
	MS-3	502	12.55	110	1380	350	4392	7700	96635	71	891
	MS-4	109	2.73	355	967	410	1117	25	68	90	245
14	E. SEEP	9.1	0.23	120	27	10	2	5	1	14	3
15	W. SEEP	14.2	0.36	49	17	100	35	5	1		
16	SWSA 6 (1&2)	0.5	0.01								
17	SWSA 6 (3)	0.7	0.02	5	0	190	3	5	0		
SUBTOTAL		635.5	15.89		2392		5550		96706		1139
18	MS-5	690	17.25							101	1742.3

<sup>a</sup> Estimated by difference or sum.

Table 2. Indicator Calculations of White Oak Creek Historical Fluxes

MAP No.	SITE	JUL & AUG VOLUME MG	MEAN FLOW RATE (CFS)	60Co CONC (Beq/Kg)	Q* C	90Sr CONC (Beq/Kg)	Q* C	137Cs CONC (Beq/Kg)	Q* C	Zn CONC (PPM)	Q* C
1	MS-2	351.3	8.78	5	44	23	202	10	88	150	1317
2	PWTP	12.4	0.31								
3	3RD ST	363.7	9.09	160	1455	220	2000	26000	236405	150	1364
4	STP	15.6	0.39								
5	NWT-U	7.0	0.18	5	1	80	14	5	1	4	1
6	FIRST CR.		2.50	5	12	580	1450	12	30		
7	NWT-D		2.68	5	13	300	804	345	925	105	281
	SUBTOTAL	386.3	12.16		1468		3464		236436		1365
8	MS-2A	526.5	13.16		0		0		0	51	671
9	T-2A(BG4)	2.1	0.05	5	0	12000	630	740	39	10	1
	SUBTOTAL	528.6	13.22		0		630		39		672
10	MS-3	502	12.55	110	1381	350	4393	7700	96635	71	891
	MB/HFIR (EST'D)		0.9	25300	22770	10	9	140	126	207	186
11	MS-4A	72.1	1.80	4000	7210	10	18	26	47	220	397
12	MS-4B	9.3	0.23	12	3	1140	265	20000	4650	19	4
	SUBTOTAL	81.4	2.03		7213						
13	MS-4	109	2.73	350	954	350	954	23	63	90	245
10	MS-3	502	12.55	110	1381	350	4393	7700	96635	71	891
13	MS-4	109	2.73	350	954	350	954	23	63	12	33
	T7 SEEP		0.10								
	T7 WEST		0.10								
14	E. SEEP	9.1	0.23	120	27	10	2	5	1	14	3
15	W. SEEP	14.2	0.36	49	17	100	36	5	2	4	1
16	SWSA 6 (1&2)	0.5	0.01								
17	SWSA 6 (3)	0.7	0.02	5	0	190	3	5	0	3	0
	SUBTOTAL	635.5	15.89		2379		5387		96701		928
	WOC/WOL	690	17.25	3200	55200	280	4830	50000	862500	101	1742



**QUARTERLY REPORT: 15 APRIL, 1986**

**INVESTIGATION OF BEDLOAD TRANSPORT OF CONTAMINATED GRAVEL  
IN THE WHITE OAK CREEK DRAINAGE  
SUBCONTRACT NO. 19X-27463 C**

**THURE E. CERLING  
DEPARTMENT OF GEOLOGY AND GEOPHYSICS  
UNIVERSITY OF UTAH  
SALT LAKE CITY, UTAH 84112**

**MAJOR ELEMENT CHEMISTRY OF STREAMS AND METAL  
CONTAMINATION IN THE WATERSHED**

**INTRODUCTION**

Two previous reports have detailed the collection of samples from White Oak Creek Basin in July and August, 1985 that were to be used to determine the status of contamination in that basin, and a discussion of radionuclide contamination in White Oak Creek Basin. This report presents a preliminary interpretation of changes in stream chemistry due to the ORNL activities and a discussion of the metal content of sediments in the basin.

Briefly, a collection of stream water samples was made to estimate the chemistry of the streams in the drainage basin. It is well known that almost any of the activities of industrialized man results in changes to stream chemistry. It is the purpose of this section to examine the changes in the White Oak Creek Basin to quantify changes in the major element chemistry of the streams.

A second important issue is that of the concentration of metals in the basin. Metal contamination is also an important result of industrial activities and thus it is important to document the potential of contamination of the watershed by metals.

Thus this report will address several issues: 1) changes in stream water chemistry due to ORNL activities, 2) preliminary characterization of sediments in the basin, and 3) metal contamination in the basin.

At University of Utah, this work has been done with the assistance of C. Pittlekow and D. Ackerman. Chemical and radionuclide analyses have been done in conjunction with B.R. Clark and T.G. Scott, respectively.

### A. CHANGES IN STREAM WATER CHEMISTRY IN THE BASIN.

Samples of stream water were collected from the primary sampling sites (Sites 1 - 17) on 13 August, 1985 (Figure 1). Samples 5661 through 5664 were collected in the morning of 13 August, samples 5665 to 5674 and 5681 were collected in the afternoon of 13 August. Alkalinity was measured within 4 hours after collection for each of the samples; cations were analyzed by atomic absorption, anions by ion chromatography, and silica by ICP.

Background samples. It is useful to discuss water samples that represent a minimum of anthropogenic input. These two samples are 5661 and 5681. Sample 5661 was collected at Site 10 (Figure 1) near the headwaters of White Oak Creek and is representative of waters derived primarily from the Knox dolomite. Significantly, it is a water dominated by  $\text{Ca-Mg-HCO}_3$ : the  $\text{Ca:Mg}$  ratio approaches 1 which would be expected in a water derived from the weathering of dolomite. Sample 5681 (Site 17) predominantly drains the Conasauga Shale in upper Melton Branch. It is a water dominated by  $\text{Ca-HCO}_3$ : much less magnesium is present because comparatively little dolomite is present in the drainage basin. Because of extensive weathering of the shale, this water appears to be a primarily a result of dissolution of carbonates that are present in the Conasauga Shale.

The important characteristics of both of these waters is that  $m_{\text{Ca}^{+2}} + m_{\text{Mg}^{+2}} \gg m_{\text{Na}^+} + m_{\text{K}^+}$ ,  $m_{\text{HCO}_3^-} \gg m_{\text{Cl}^-} + m_{\text{SO}_4^{2-}}$ , and  $m_{\text{NO}_3^-} < 0.1$  mmole per liter (in the ensuing discussion, charges will be omitted from the ions). While no water samples were collected from an undisturbed part of the basin draining only Chicamauga limestone it is likely that it has a water composition similar to sample 5681 which is controlled by limestone dissolution. Sample 5674 taken at the staff gauge in Northwest Tributary may have a composition similar to the background; however because it is downstream of plant effluents it is likely to be at least slightly altered. The higher chloride values suggest this as well.

Comparison of other water samples suggests that only sample 5671 from SWSA 6 has a chemistry that is comparable to the background values. All other samples have a chemistry that is significantly different, usually higher in Na, alkalinity, Cl,  $\text{SO}_4$ , and  $\text{NO}_3$ . This will be discussed below.

Anthropogenically affected samples. There are several approaches to understanding the changes in chemistry of waters resulting from anthropogenic activities. Diagrammatically, these can be shown in several

ways. These include triangular diagrams to illustrate the changes in the proportions of dissolved species; this shows the relative importance of dissolved for mineral reactions. The first of these is to plot  $\text{SiO}_2$ , alkalinity, and  $\text{SO}_4 + \text{Cl}$  at the three apexes. Figure 2 shows that there is an important increase in the relative amounts of  $\text{SO}_4 + \text{Cl}$  for many of the waters in the basin. Examination of the anions in more detail can be accomplished by examination of a diagram with  $\text{SO}_4$ ,  $\text{Cl}$ , and  $\text{NO}_3$  at the apexes. In spite of the real increase in  $\text{SO}_4$  and  $\text{Cl}$ , this diagram (Figure 3) shows an important increase in the amount of  $\text{NO}_3$  present in the waters. This is not accompanied by a noticeable increase in  $\text{PO}_4$ . Examination of cation ratios show that the effect of the ORNL activities is to greatly increase the proportions of Na with respect to Ca and Mg (Figure 4). Lastly, one can compare each of the ions in White Oak Creek at Monitoring Station 3 (5668) to the headwater sample (5661); and that in Melton Branch at Monitoring Station 4 (5667) to the headwater sample (5681). Figure 5 shows that Na, alkalinity,  $\text{SO}_4$ ,  $\text{Cl}$ , and  $\text{NO}_3$  show major increases as a result of ORNL activities, and suggest that the anthropogenic component for each of these is on the order of 90%, 80%, 90%, and 90% respectively. This suggests that ORNL activities have greatly altered stream chemistry. Such a finding is similar to that for the Rhine River (Stumm and Morgan, 1981).

Another interesting observation of this study concerns the downstream change in chemistry between the sample taken at the Third Street Bridge (5662) and that taken at Monitoring Station 2A (5673). The former sample was taken in the morning about 1100 hours, while the latter was collected at about 1530 hours. The drastic change in chemistry between these two samples may result from an differing plant effluent releases in the afternoon compared to those in the morning.

#### PRELIMINARY NOTES ON THE CHARACTERIZATION OF SEDIMENTS IN WHITE OAK CREEK BASIN.

In this survey, several hundred samples of gravel were collected from the basin. The White Oak Creek Basin occupies several different valleys each of which has different bedrock lithologies exposed. The Knox dolomite and the Chicamauga Limestone outcrop extensively in Bethel Valley, while the Conasauga Shale outcrops extensively along Melton Branch. The two valleys are separated by a steep outcrop of the Rome Formation. The southern valley wall of Melton valley is the Knox dolomite. Previous studies (Cerling and Spalding, 1980; 1982) have shown that important properties of

the sediments such as distribution coefficients ( $K_d$ ) are quite different in different parts of the watershed. Because distribution coefficients can be very important in using the sediment concentrations of radionuclides to calculate the equilibrium water radionuclide concentrations, additional characterization of the sediments is required. This section discusses some observations on the the mineralogy and sediment petrology of samples collected from the basin as part of this study.

Petrography. Nineteen sediment samples from the basin were examined in detail. Thin sections were made of each of these and observations were made on 78 to 154 grains for these samples. The petrographic categories were:

Chert

1. Silicified fossil and/or oolitic limestone: major silica replacement of fossiliferous and/or oolitic limestone
2. Silicified dolomite: major silica replacement of dolomite demonstrating a rhombohedral pattern
3. Chert: includes chert, chalcedony, microquartz, and megaquartz

Carbonate

4. Limestone: any carbonate not showing definite signs of fossils, oolites, or dolomite
5. Fossiliferous and/or oolitic limestone: any carbonate showing fossils and/or oolites without significant replacement by dolomite
6. Dolomite: a carbonate demonstrating high relief rhombohedrons

Shale: litharenite

7. Silty shale: over 75% clays with a linear fabric such that birefringence between clay minerals is similarly oriented
8. Moderately sorted siltstone: moderate sorting with a large clay and lithic fraction, a poor linear fabric discernable
9. Poorly sorted siltstone: poor sorting with a large clay and lithic fraction, poor linear fabric discernable

Shale: sublitharenite

10. moderately sorted siltstone: moderate sorting with less than 25% clays and lithics

11. poorly sorted siltstone: poor sorting with less than 25% clays and lithics

Other:

12. Heavy to complete Fe-Mn coatings: grains that could not be confidently identified due to extreme Fe/Mn coating
13. Unable to identify or classify: extremely unusual or odd fragments, including what appears to be metamorphic quartz

Estimates of the amount of Fe/Mn coatings were made by observation the presence or absence of coating on either end of the longest and shortest axes of the sediment grains (four observations per grain). These were then tallied and averaged for each sediment type.

The high abundance of chert and limestone in Bethel Valley is reflected by the relatively low distribution coefficients for  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ . This difference is important in considering the extractable metal contents of sediments because limestone has different background concentrations of some metals than does shale.

Manganese and iron rich coatings were examined as well. Fe/Mn coatings formed on plate glass, glass beads, or PVC pipe were examined by X-ray diffraction and by the SEM. XRD suggested that the phase formed was either todokorite or birnessite: diffraction patterns were indistinct because of the poorly crystalline nature of the coatings. Qualitative EDAX observations on the SEM suggested that the coatings contained Mn, Fe, Ni, Co, and Cr. Observations of extractable metals suggest that all of these are mobile in the basin to some degree (discussion below).

#### DISTRIBUTION OF METALS WITHIN THE BASIN

An important aspect of this study is to determine the distribution of metals in the sediments within the basin within the context of contamination of stream sediments by ORNL activities. A previous report indicated that Zn, P, and possibly Cu were actively being discharged into waters of White Oak Creek Basin. These elements were shown to be of immediate importance because sediments placed in the streams downstream from cooling water effluents (south of 4500S and HFIR) had a significantly higher concentration of these metals after one month than they had at the beginning of the experiment. Longer term (one year) samples placed in the streams will provide an answer to the active nature of other metals. Extraction was by hydroxylamine-hydrochloride as outlined in a previous

report (Cerling, 1985, 1986).

However, an examination of the extractable metal content of indigenous gravels in the watershed can still provide some preliminary estimates of the magnitude of potential metal contamination. Table 3 and Figures 6 through 20 show the extractable metal contents for Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, P, V, and Zn. Several other metals were analyzed as well, but they showed little variation within the basin. The distribution of each of these metals will be discussed in turn.

Aluminum. Extractable aluminum has only slight variation in the entire watershed. The lowest values are in Bethel valley which has the lowest shale content.

Barium. Barium varies little throughout the basin. In fact, one of the background sites (Site 17) is among the highest in extractable barium.

Calcium. Calcium was mapped to show the dependance on carbonate values. Samples with the highest carbonate values (Table 2) also have the highest extractable calcium. Most of these samples are in Bethel Valley. Interestingly, one sample outside of Bethel Valley with high extractable calcium (Site 5) has about 30% carbonate fragments. This may be a result from gravel associated with the roads in the area which have a limestone base.

Cadmium. Only a few samples have higher than background cadmium values: all of these are in White Oak Creek or the Northwest Tributary. However, the known association of cadmium with calcium carbonate suggests that this may be an artifact of sampling bias created by differing bedrock compositions.

Cobalt. There is no definite pattern to the distribution of cobalt in the basin. One of the highest observed values is from the locality chosen for a representative background sample. Cobalt does not appear to be correlated with the amount of manganese coating on the sediments.

Chromium. Background chromium levels seem to be about 1 or 2 ppm. All samples with values significantly higher than this (>10 ppm) are associated with known Zn contamination: ORNL lab complex and HFIR which attain average values as high as 16 ppm. As with Zn, the Cr contamination in the ORNL laboratory complex may be associated with the cooling effluent south of Building 4500S. In addition, there is a suggestion of chromium input by the NSPP and MSRE areas. There is no evidence for chromium input from any of the SWSA areas.

Copper. Background values for copper appear to be about 0.5 ppm. Again,

the known areas of Zn contamination (ORNL lab complex and HFIR) show the highest copper values (up to 9 ppm) which are more than 10 times the background value. The only significant Cu value associated with the SWSA region is from SWSA 6 on the east side. This should be examined further since this area showed evidence for  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  contamination, as well.

Iron. Iron is ubiquitous in the near surface environment. It is leached from sediments in slightly reducing conditions and precipitated in oxidizing portions of streams (Cerling and Turner, 1982). Variations in iron are most likely related to the interaction between groundwater input (high Fe content) into streams, and the relative stream velocity which can abrade Fe/Mn coatings.

Magnesium. Magnesium values are similar throughout much of the basin, the one exception being Site 5. The reason for this is not clear. However, Mg is not a toxic metal.

Manganese. The distribution of manganese in the basin varies only slightly. Like iron it is mobilized in slightly reducing conditions (such as groundwater) and is readily fixed in oxidizing portions of streams. The extractant chosen is an excellent extractant for manganese and should extract those metals associated with Fe/Mn coatings.

Molybdenum. Background molybdenum values are about 0.5 ppm. The values significantly above background appear to be associated with the ORNL lab complex and HFIR. In addition, SWSA 4 appears to have high Mo values (7 ppm).

Nickel. Background nickel values seem to be about 5 ppm. Only one site has significantly higher values than background. This is SWSA 4 which has average values at least 50 times the background value.

Phosphorus. It was previously pointed out that phosphorus was an active input to the White Oak Creek system by the ORNL lab complex and by HFIR. Observations of extractable P from indigenous gravel confirms this previous observation.

Vanadium. No discernable differences in vanadium distribution are observed in the White Oak Creek Basin.

Zinc. The previous report showed that zinc was actively being input into the White Oak Creek system. Background values are about 5 ppm and values 30 to 70 times this are observed associated with the ORNL lab complex and HFIR.

In summary, observations of metal distributions in White Oak Creek drainage confirm the previous observations that some metal contamination

is taking place. This study suggests that significant Cr, Cu, Mo, P, and Zn are being discharged into White Oak Creek and these metals are being absorbed onto the sediments. The principle points of discharge appear to be the ORNL laboratory complex and HFIR, with minor discharge from the NSPP and MSRE areas. In addition, there appears to be significant Mo and Ni discharge from SWSA 4.

Although cadmium levels are slightly higher in Bethel Valley, this may be attributed to the high limestone content of the stream gravels.

#### SUMMARY

Several important observations come out of this portion of the study. First, the chemistry of White Oak Creek and Melton Branch are significantly changed by the activities of ORNL. The sodium, chloride, sulfate, and nitrate fluxes are considerably enhanced. This is typical of anthropogenic changes to rivers in any region and is probably not of a significant nature. Second, the metal contribution of ORNL is measureable for the metals Cr, Cu, Mo, Ni, P, and Zn. Again, this is typical of industrial outputs (Salomons and Forstner, 1984) although the levels should probably be further quantified.



## REFERENCES

- Cerling, T.E., 1985, Investigation of bedload transport of contaminated gravel in the White Oak Creek Drainage. Survey of sediments in White Oak Creek Drainage: Field Operations. Quarterley Report to Oak Ridge National Laboratory.
- Cerling, T.E., 1986, Investigation of bedload transport of contaminated gravel in the White Oak Creek Drainage. Status of active contamination in the White Oak Creek Watershed: metals and radionuclides. Quarterley Report to Oak Ridge National Laboratory.
- Cerling, T.E. and B.P. Spalding, 1981, Areal distribution of  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ , and  $^{90}\text{Sr}$  in streambed gravels of White Oak Creek watershed, Oak Ridge, Tennessee. ORNL/TM-7318, Oak Ridge National Laboratory, Oak ridge, Tennessee.
- Cerling, T.E. and B.P. Spalding, 1982, Distribution and relationship of radionuclides to streambed gravels in a small watershed. *Environmental Geology*, v. 4, p. 99-116.
- Cerling, T.E. and R.R. Turner, 1982, Formation of freshwater Fe-Mn coatings on gravel and the behavior of  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ , and  $^{137}\text{Cs}$  in a small watershed. *Geochimica Cosmochimica Acta* v. 46, p. 1333-1343.
- Glover, E.D., 1977, Characterization of a marine birnessite. *American Mineralogist*, v. 62, p. 278-285.
- McMaster, W.M. and H.D. Waller, 1965, Geology and soils of Whiteoak Creek Basin, Tennessee. ORNLTM-1108, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Potter, R.M. and G.R. Rossman, 1979, Mineralogy of manganese dendrites and coatings, *American Mineralogist*, v. 64, p. 1219-1226.
- Potter, R.M. and G.R. Rossman, 1979, The tetravalent manganese oxides: identification, hydration, and structural relationships by infrared spectroscopy. *American Mineralogist*, v. 64, p. 1199-1218.
- Salomons, W. and U. Forstner, 1984, *Metals in the Hydrosphere*. Springer-Verlag, Berlin.
- Spalding, B.P. and W.J. Boegly, 1985, ORNL Radioactive Liquid Waste Disposal Pits and Trenches: history, status, and closure characterization needs. ORNL/CF-85/70. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Spalding, B.P. and T.E. Cerling, 1979, Association of radionuclides with

- streambed sediments in White Oak Creek Watershed. ORNL/TM-6895, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Stockdale, P.B., 1951, Geologic conditions at the Oak Ridge National Laboratory (X-10) area relevant to the disposal of radioactive waste. ORO-058, U.S. Atomic Energy Commission, Oak Ridge, Tennessee.
- Stumm, W. and J.J. Morgan, 1981, Aquatic Chemistry. Wiley-Interscience, New York.
- Turner, S. and P.R. Buseck, 1981, Todokorites: a new family of naturally occurring manganese oxides. Science v. 212, p. 1024-1027.
- Webster, D.A., 1976, A review of hydrologic and geologic conditions related to the radioactive solid-waste burial grounds at Oak Ridge National Laboratory, Tennessee. U.S. Geol. Surv. Open-File Report 76-727.

Figure 1. Location map showing sampling sites in White Oak Creek Basin.

Figure 2. Diagram showing relative proportions of dissolved alkalinity,  $\text{SiO}_2$ , and  $\text{SO}_4+\text{Cl}$  streams in White Oak Creek Basin.

Figure 3. Diagram showing relative proportions of dissolved alkalinity,  $\text{NO}_3$ , and  $\text{SO}_4+\text{Cl}$  in streams in White Oak Creek Basin.

Figure 4. Diagram showing relative proportions of dissolved Na, Ca, and Mg in streams in White Oak Creek Basin.

Figure 5. A. Comparison of background and anthropogenic water concentrations of cations in White Oak Creek Basin. B. Comparison of background and anthropogenic water concentrations of anions in White Oak Creek Basin.

Figure 6. Distribution of average extractable Al in stream sediments in White Oak Creek Basin. Values marked with an asterisk represent average values that have at least one value two times greater than or less than the other values in the average.

Figure 7. As Figure 6. For extractable Ba.

Figure 8. As Figure 6. For extractable Ca.

Figure 9. As Figure 6. For extractable Cd.

Figure 10. As Figure 6. For extractable Co.

Figure 11. As Figure 6. For extractable Cr.

Figure 12. As Figure 6. For extractable Cu.

Figure 13. As Figure 6. For extractable Fe.

Figure 14. As Figure 6. For extractable Mg.

Figure 15. As Figure 6. For extractable Mn.

Figure 16. As Figure 6. For extractable Mo.

Figure 17. As Figure 6. For extractable Ni.

Figure 18. As Figure 6. For extractable P.

Figure 19. As Figure 6. For extractable V.

Figure 20. As Figure 6. For extractable Zn.

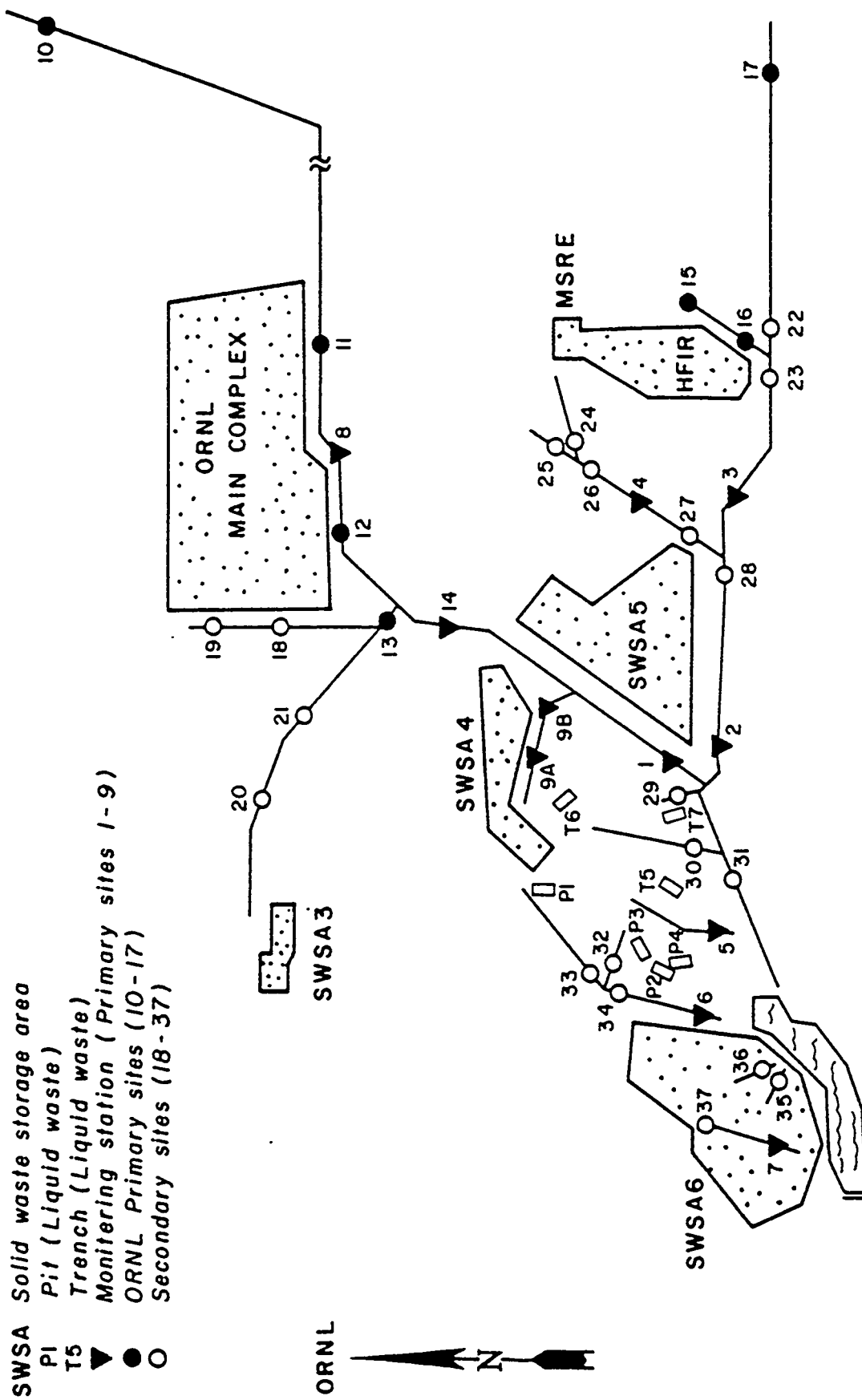


Figure 1. Location map showing sampling sites in White Oak Creek Basin.

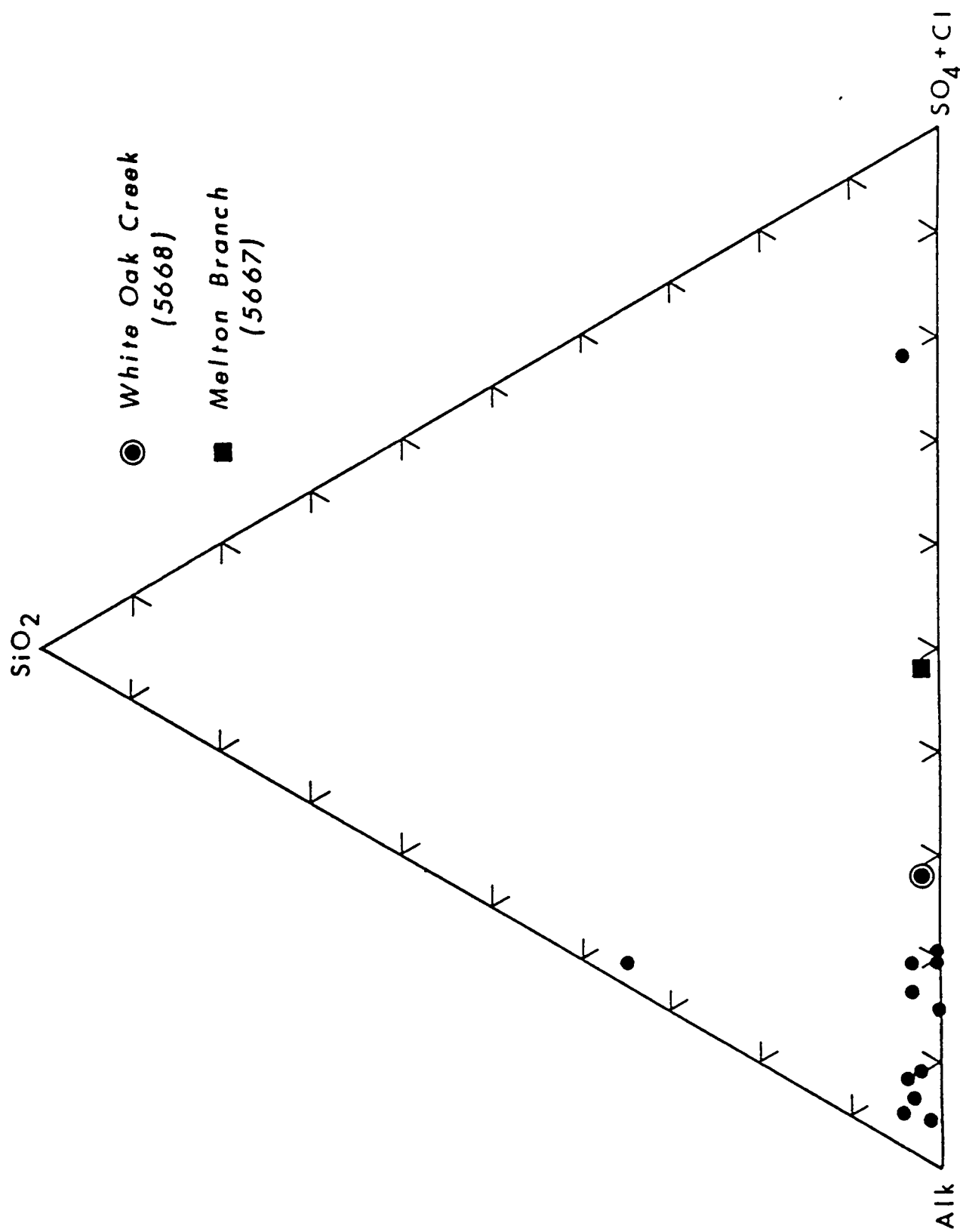


Figure 2. Diagram showing relative proportions of dissolved alkalinity,  $\text{SiO}_2$ , and  $\text{SO}_4 + \text{Cl}$  streams in White Oak Creek Basin.

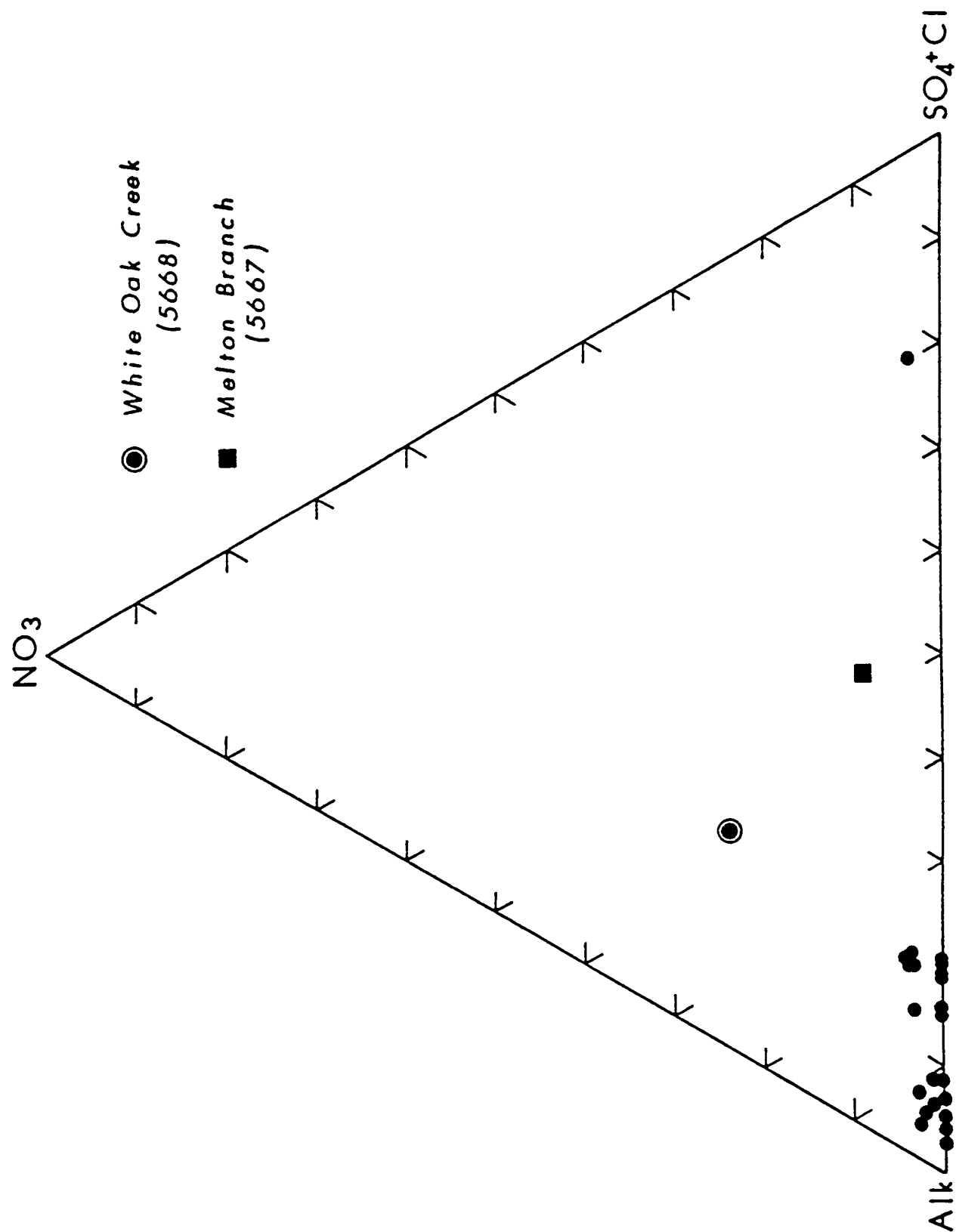


Figure 3. Diagram showing relative proportions of dissolved alkalinity, NO<sub>3</sub>, and SO<sub>4</sub>+Cl in streams in White Oak Creek Basin.

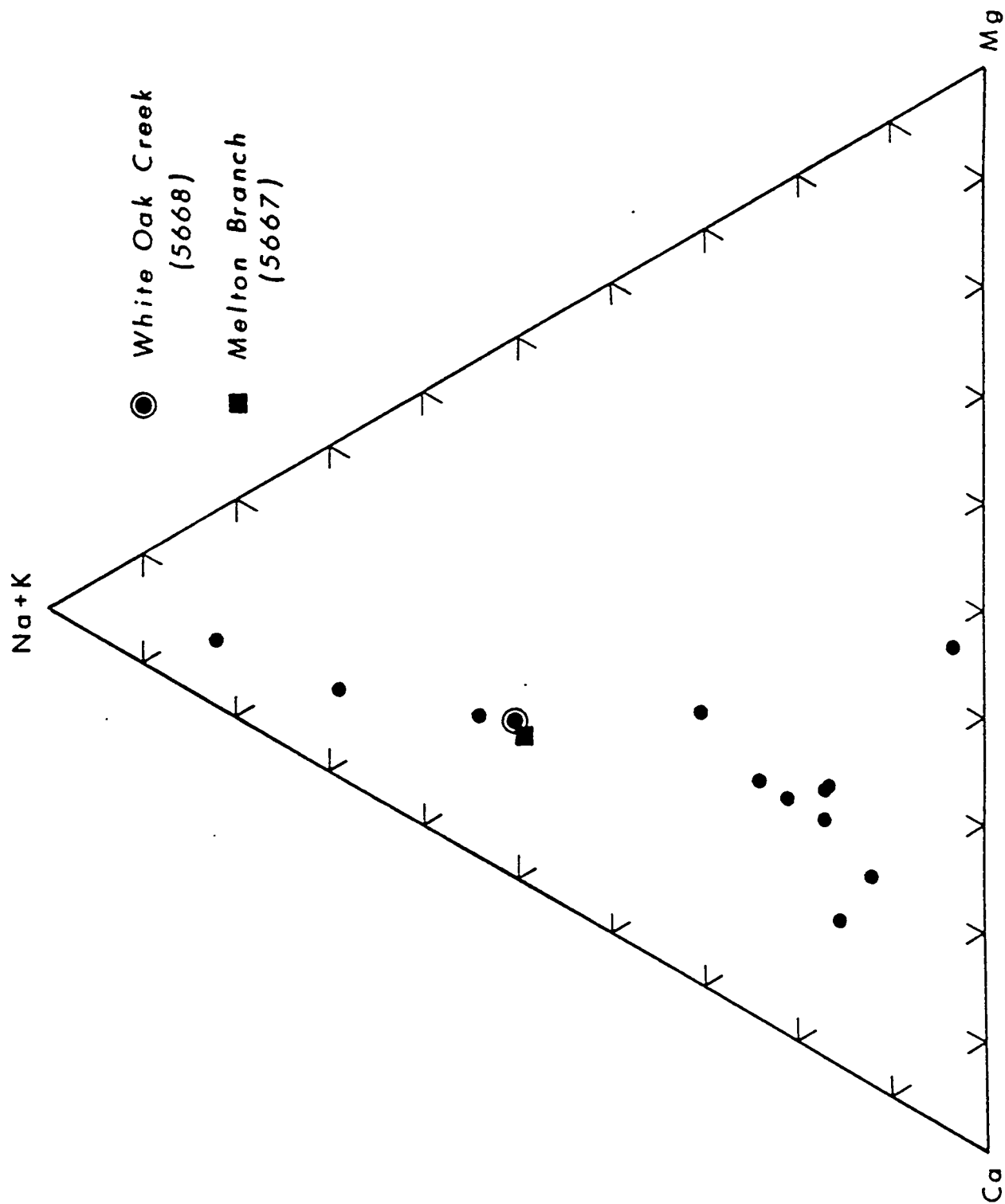


Figure 4. Diagram showing relative proportions of dissolved Na, Ca, and Mg in streams in White Oak Creek Basin.



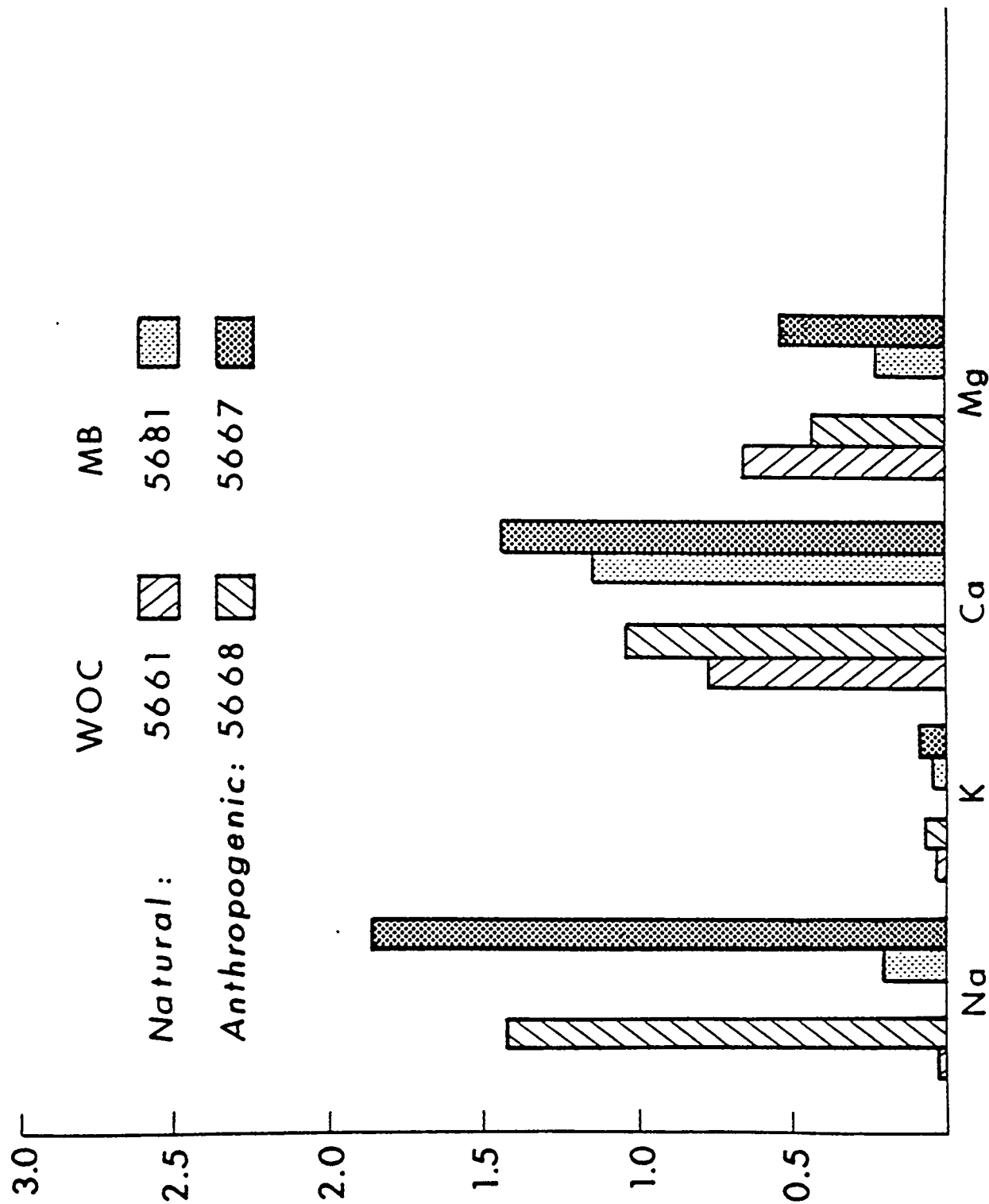


Figure 5. A. Comparison of background and anthropogenic water concentrations of cations in White Oak Creek Basin.

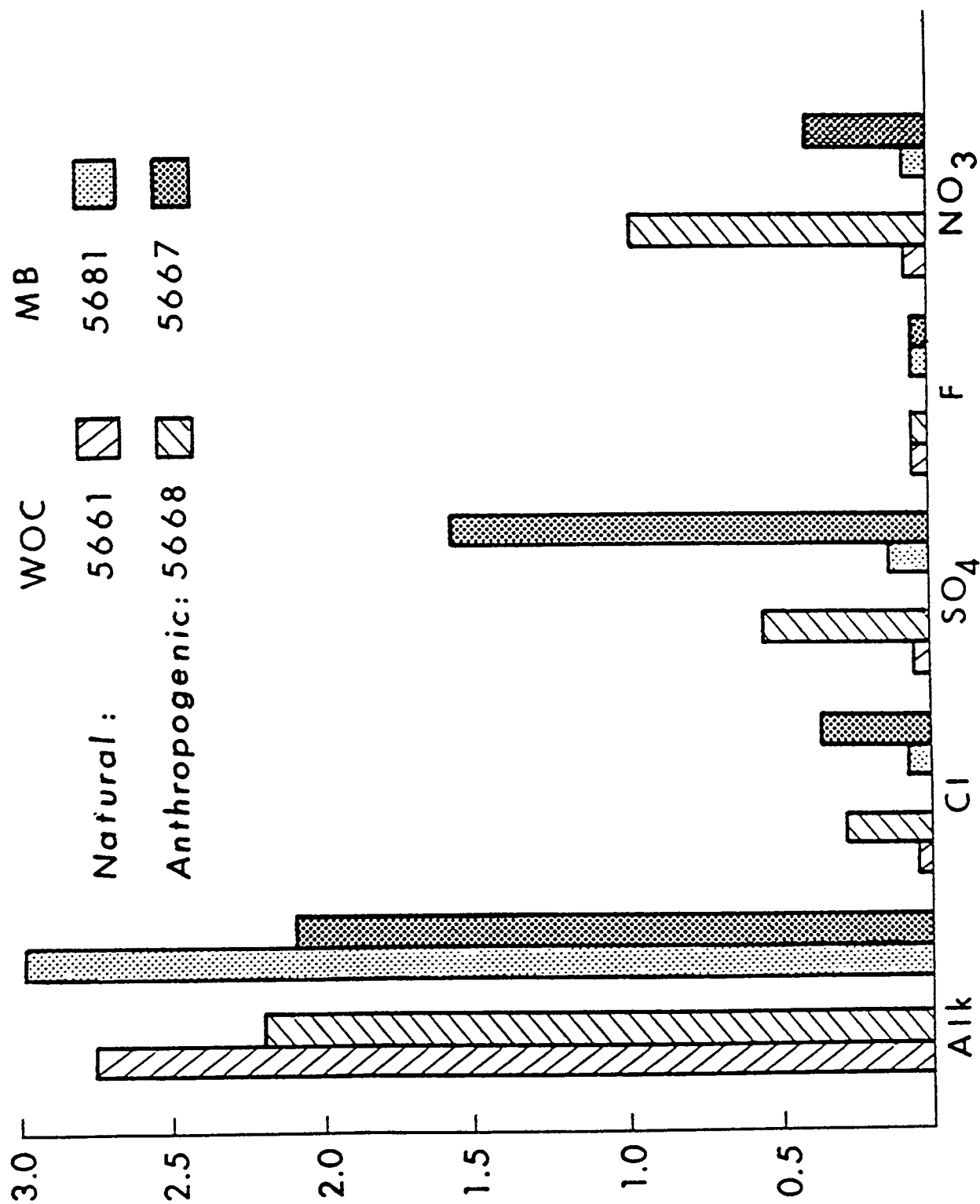
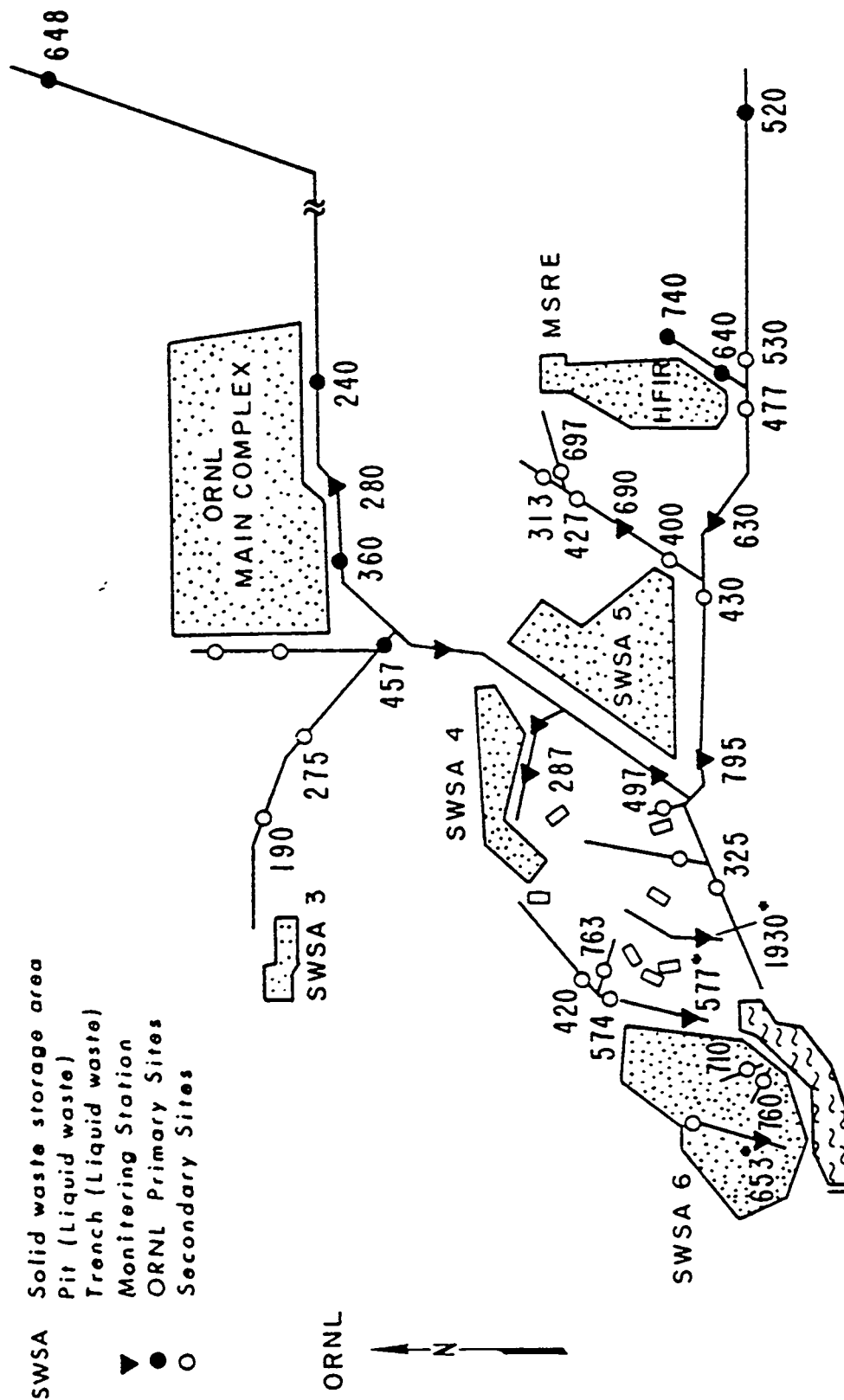


Figure 5. B. Comparison of background and anthropogenic water concentrations of anions in White Oak Creek Basin

# Extractable Al (ppm)



\* - averages contain values  
 >2x greater or less than  
 : other values in average

Figure 6. Distribution of average extractable Al in stream sediments in White Oak Creek Basin. Values marked with an asterisk represent average values that have at least one value two times greater than or less than the other values in the average.

# Extractable Ba (ppm)

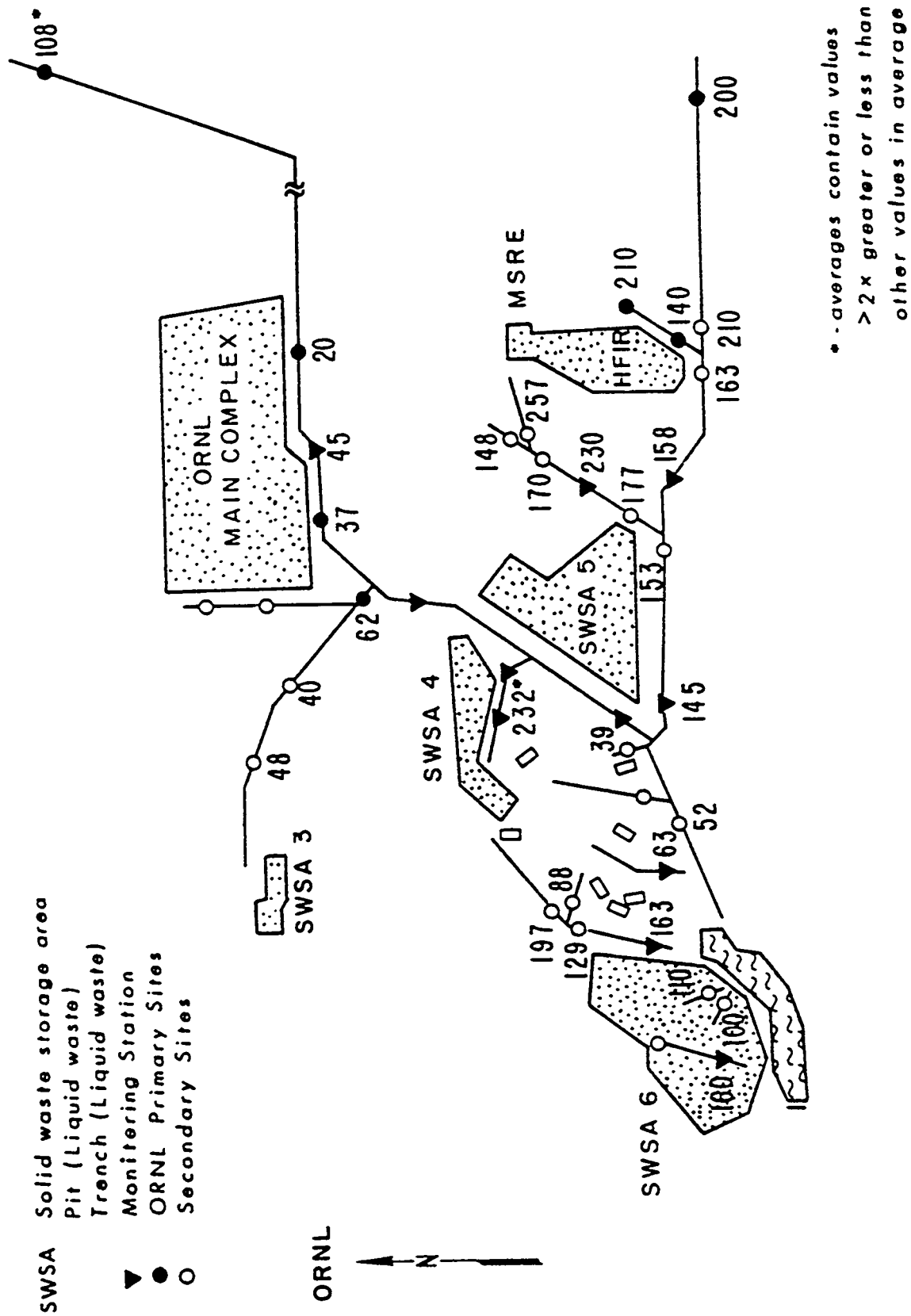


Figure 7. As Figure 6. For extractable Ba.

# Extractable Ca (ug/g)

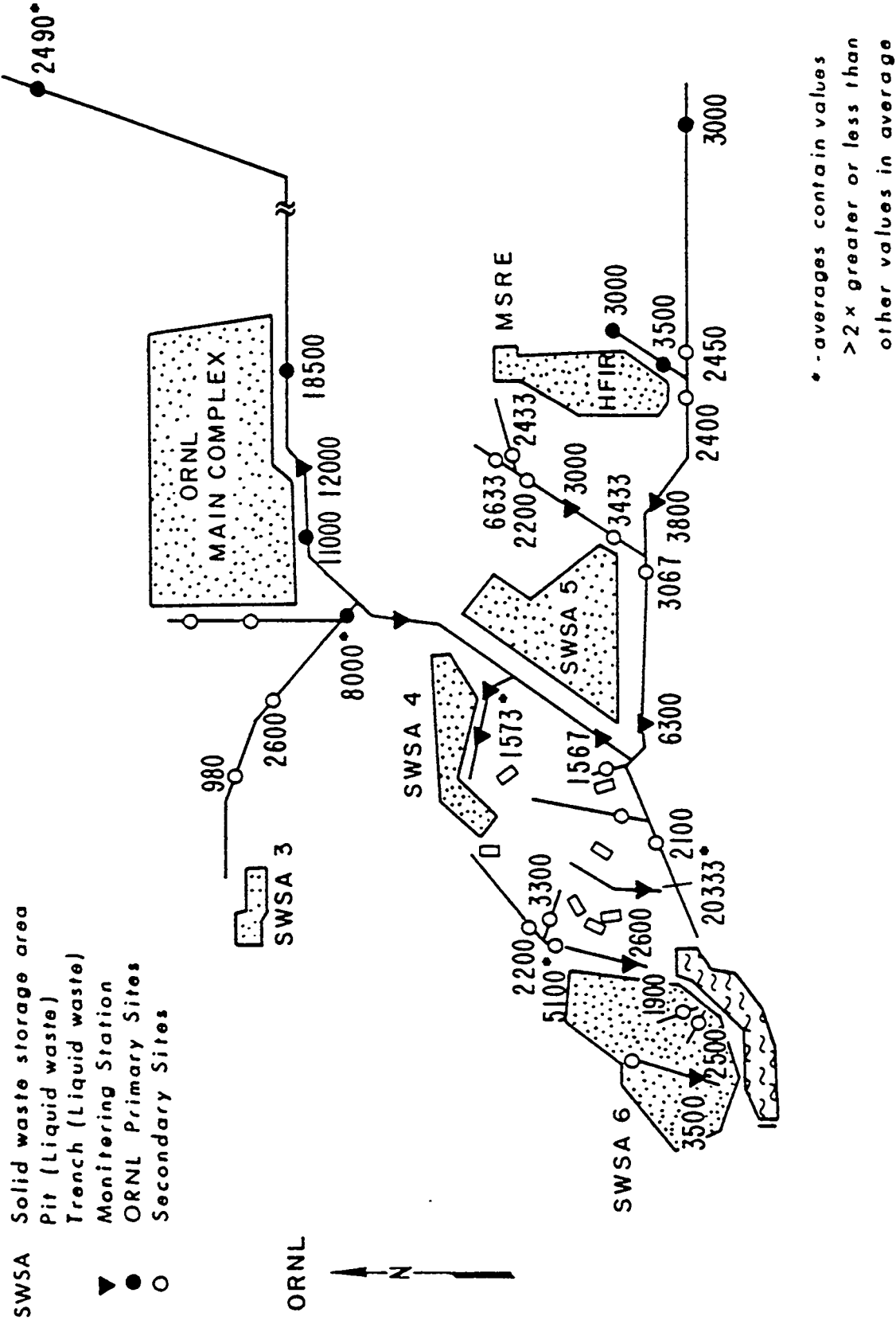


Figure 8. As Figure 6. For extractable Ca.



# Extractable Co (ug/g)

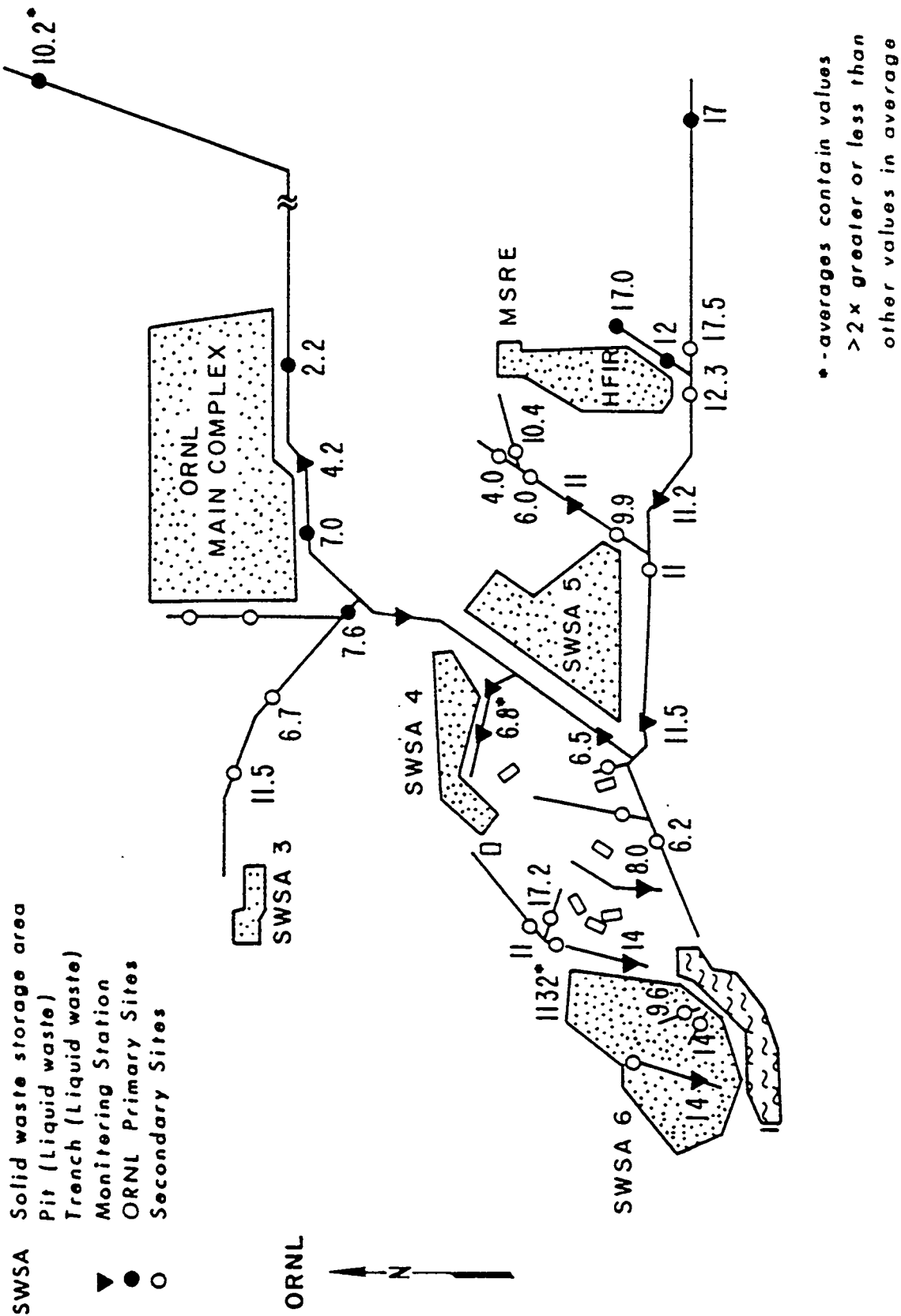
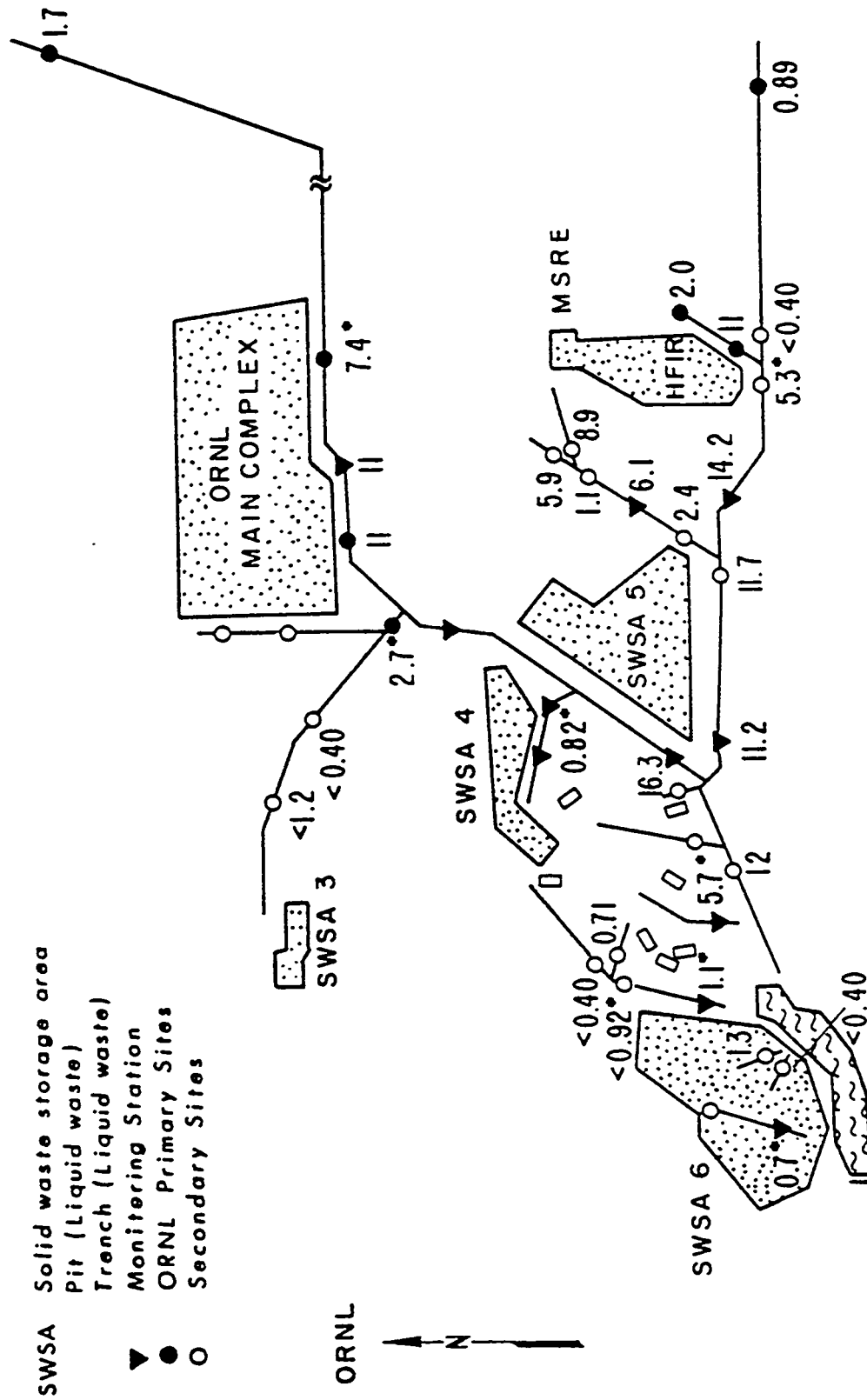


Figure 10. As Figure 6. For extractable Co.

# Extractable Cr (ug/g)

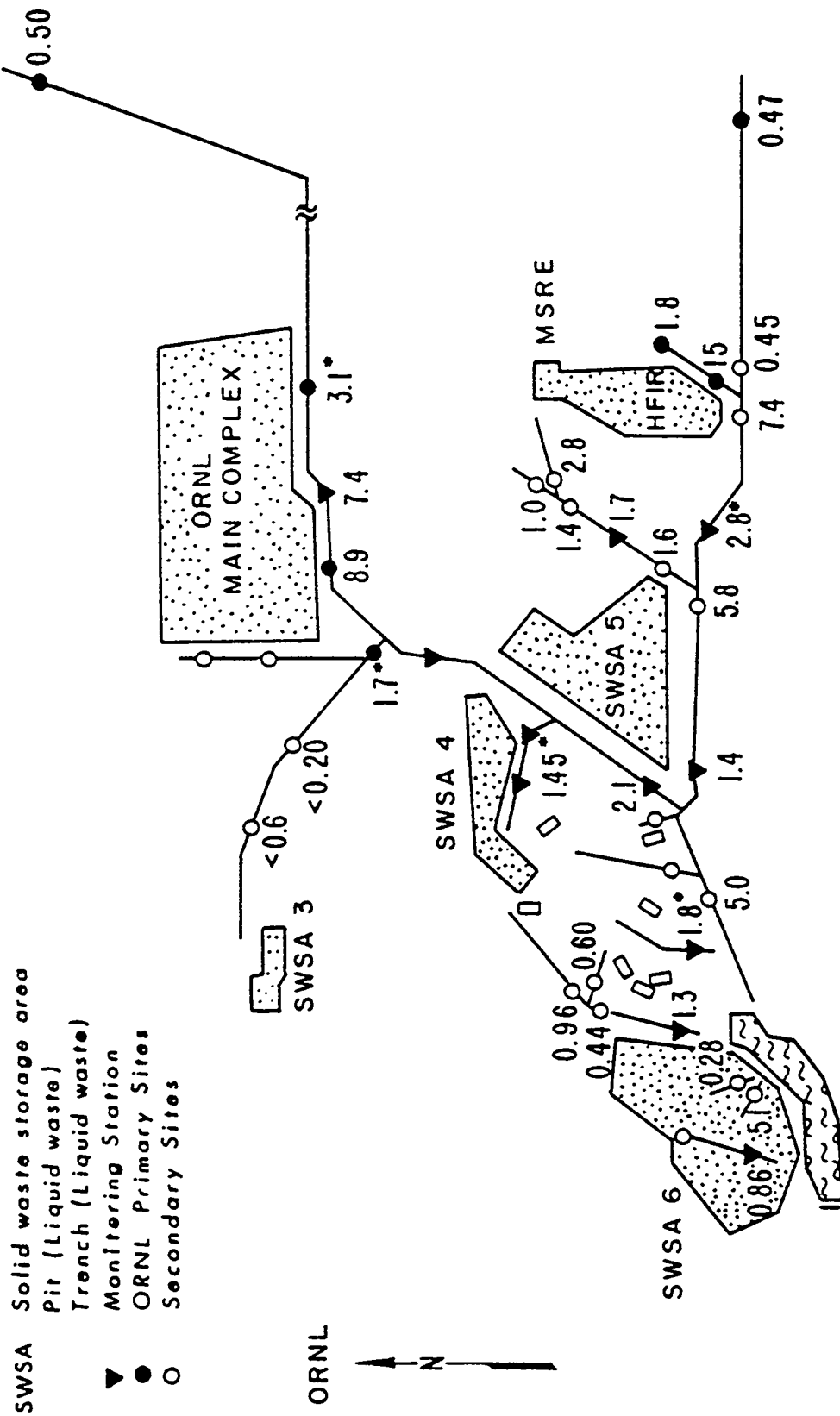


\* - averages contain values  
> 2x greater or less than  
other values in average

Figure 11. As Figure 6. For extractable Cr.



# Extractable Cu (ug/g)



\* - averages contain values  
> 2x greater or less than  
other values in average

Figure 12. As Figure 6. For extractable Cu.

# Extractable Fe (ug/g)

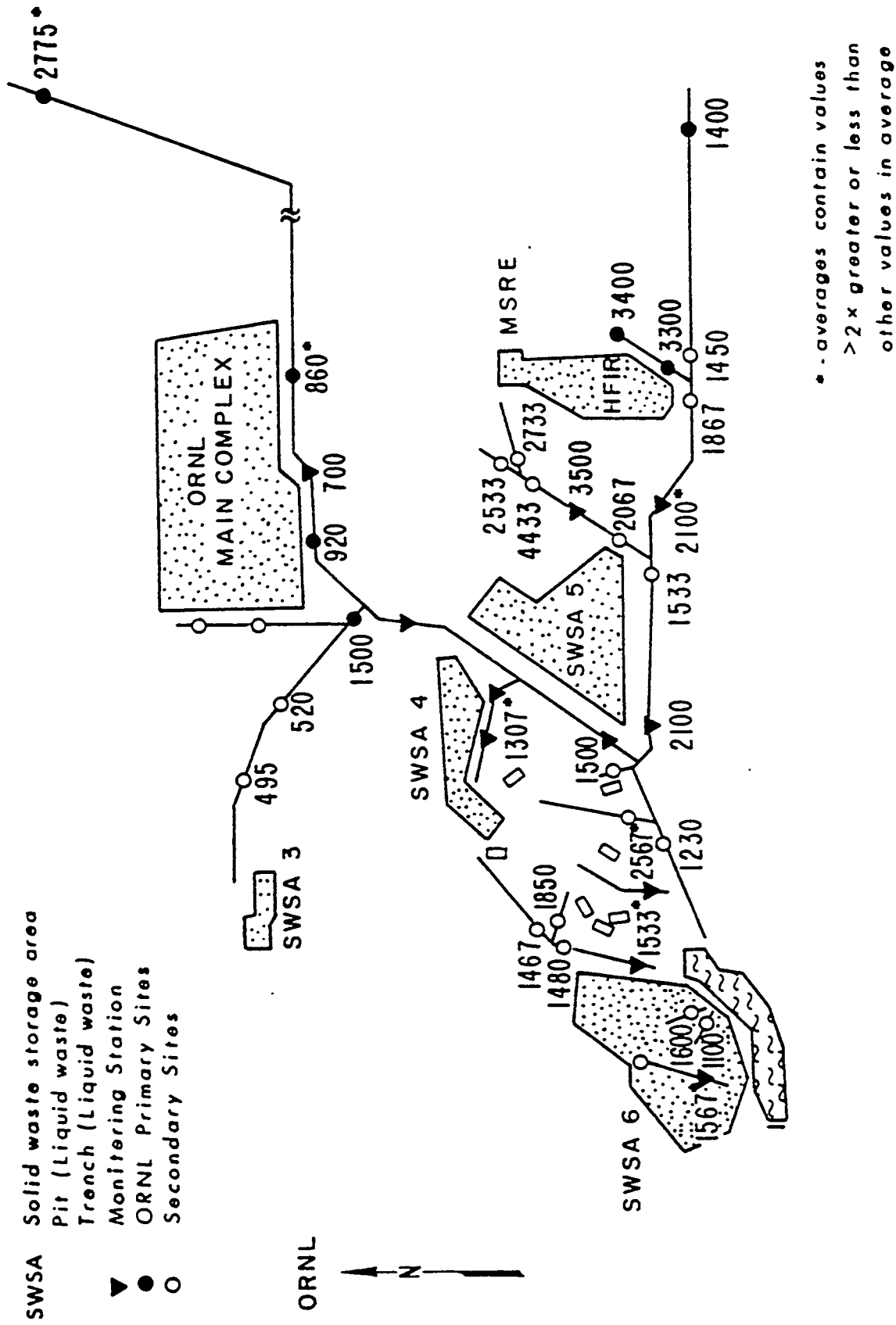
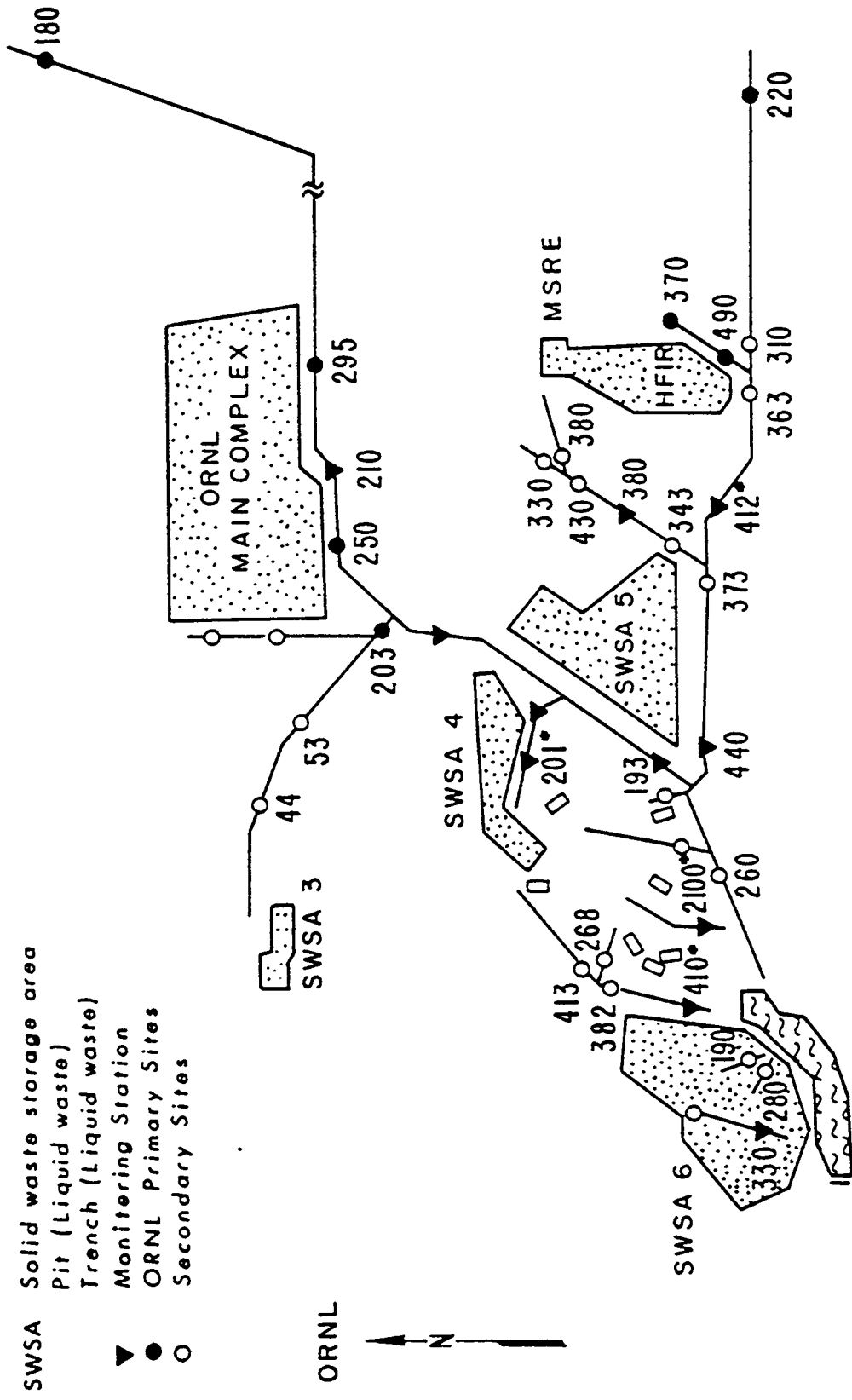


Figure 13. As Figure 6. For extractable Fe.

# Extractable Mg (ug/g)



\* - averages contain values  
 >2x greater or less than  
 other values in average

Figure 14. As Figure 6. For extractable Mg.

# Extractable Mn (ug/g)

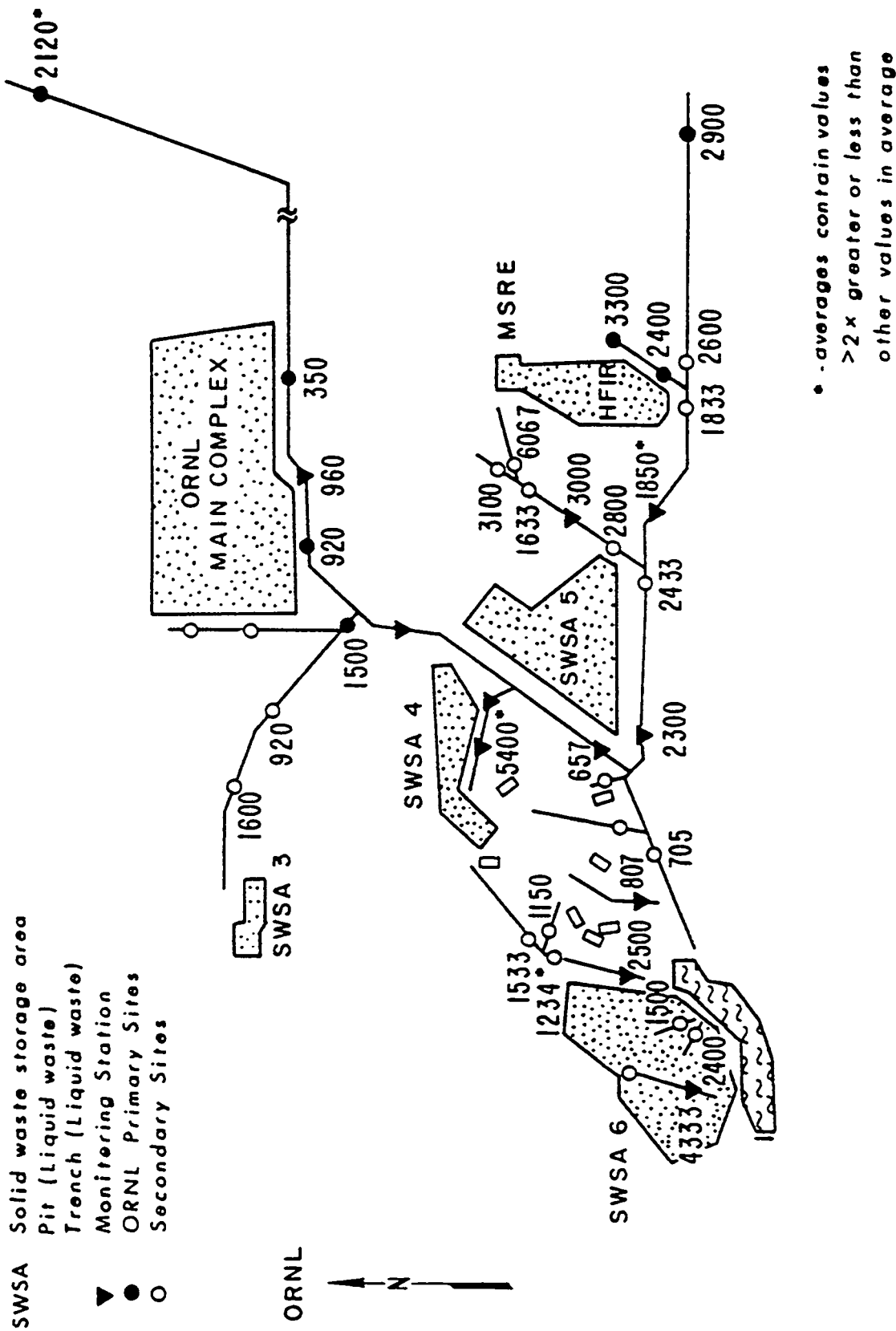
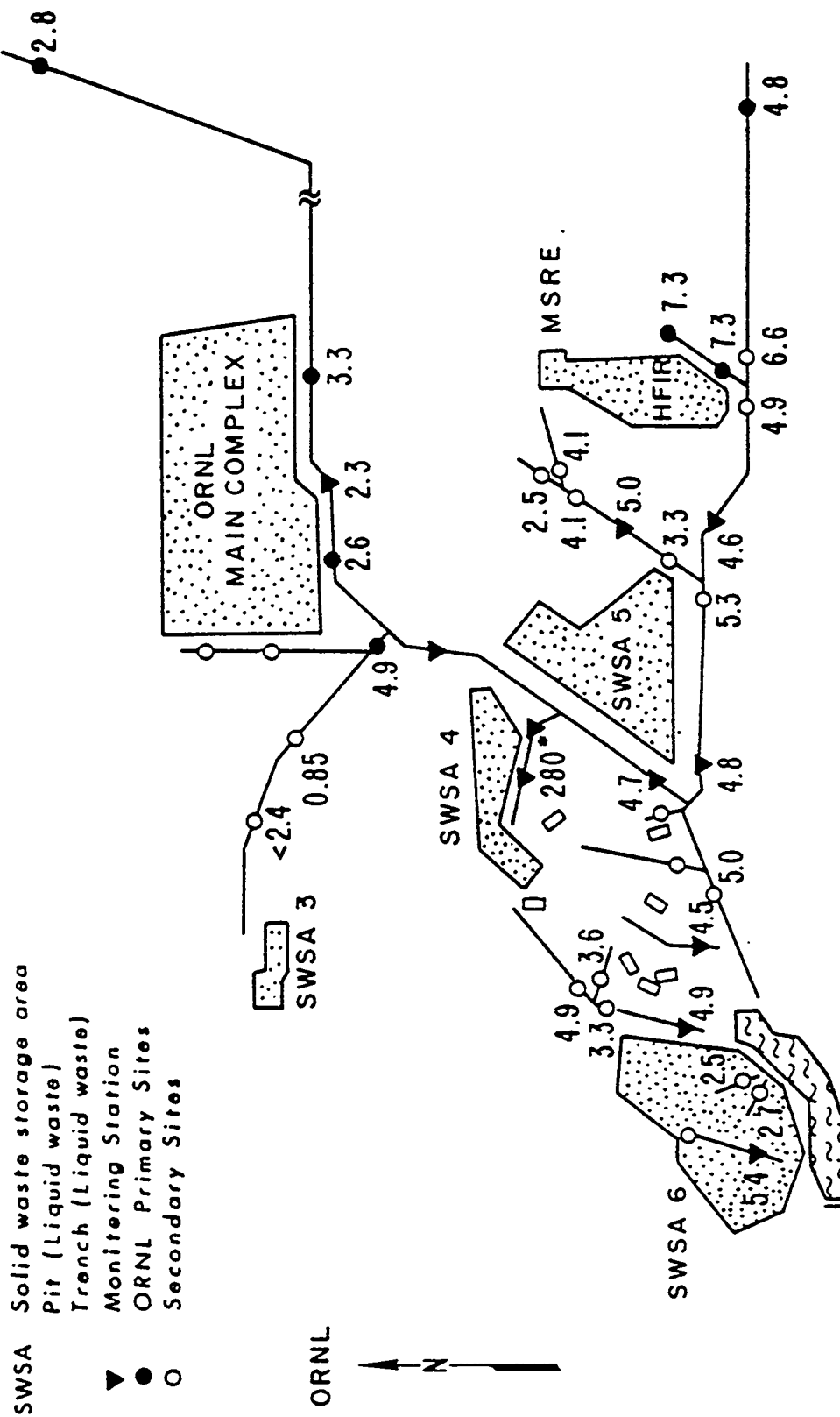


Figure 15. As Figure 6. For extractable Mn.



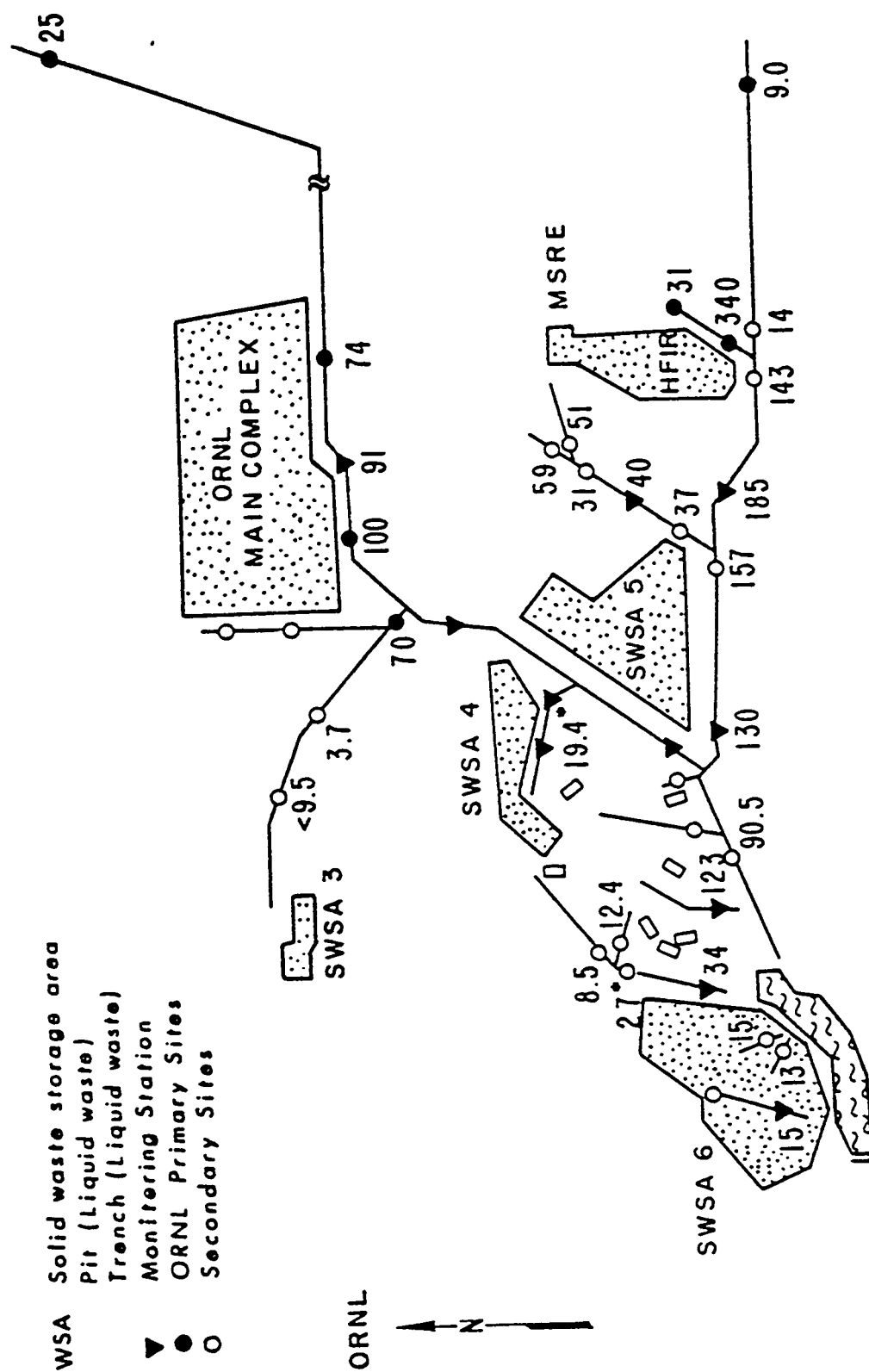
# Extractable Ni (ug/g)



\*-averages contain values  
>2x greater or less than  
other values in average

Figure 17. As Figure 6. For extractable Ni.

SWSA Solid waste storage area  
 ▼ Pit (Liquid waste)  
 ● Trench (Liquid waste)  
 ○ Monitoring Station  
 ORNL Primary Sites  
 Secondary Sites



- averages contain values  $> 2 \times$  greater or less than other values in average

Figure 18. As Figure 6. For extractable P.

# Extractable V (ug/g)

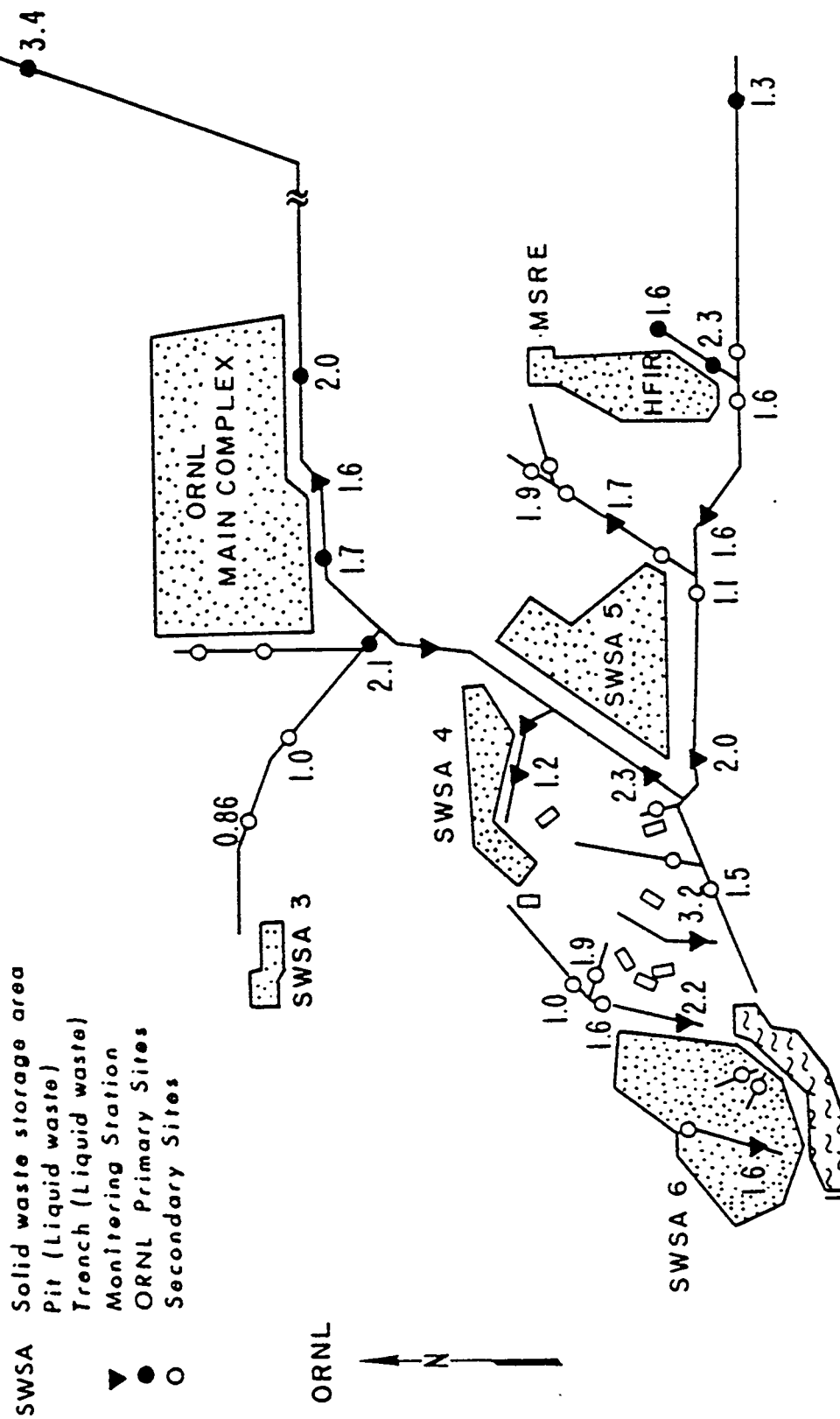
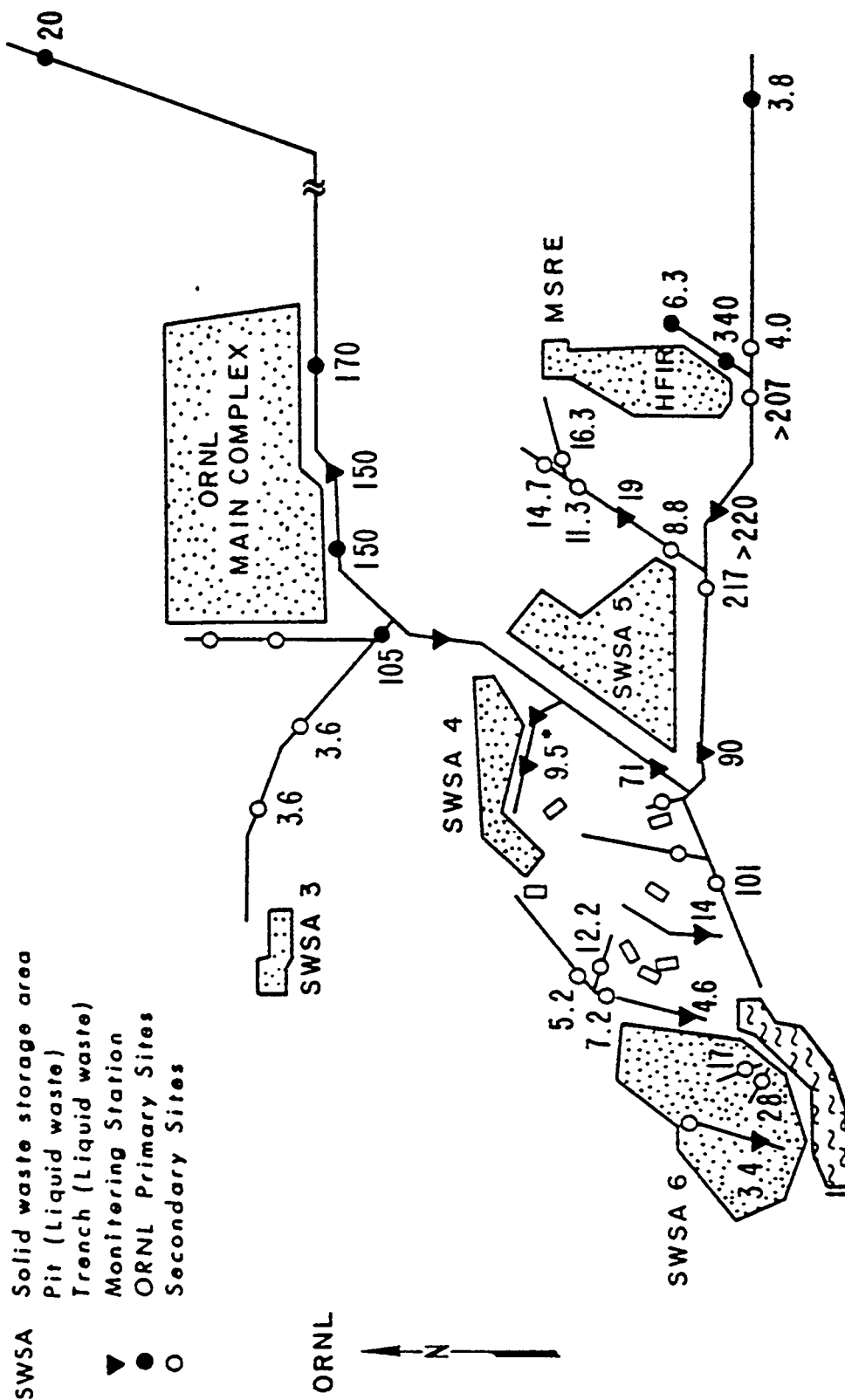


Figure 19. As Figure 6. For extractable V.



# Extractable Zn (ug/g)



\* -averages contain values  
>2x greater or less than  
other values in average

Figure 20. As Figure 6. For extractable Zn.

TABLE 1. Chemistry of waters in White Oak Creek Basin. Cations, anions and silica in mmoles per liter, except alkalinity which is in meq per liter.

	Site	pH	Na	K	Ca	Mg	Alk	Cl	SO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>2</sub>
5668	1	7.95	1.43	.06	1.04	.42	2.20	.28	.55	.97	.08
5667	2	8.15	1.87	.09	1.46	.54	2.10	.37	1.56	.40	.08
5666	3	7.66	.91	.12	2.74	1.06	1.10	.65	3.64	.21	.22
5665	4	7.79	.26	.05	1.10	.39	2.34	.20	.22	<.08	.04
5669	5	8.05	6.04	.05	.91	.43	7.00	.54	1.14	.37	.03
5670	6	7.44	3.87	.08	1.33	.46	5.97	.17	.07	.14	.08
5671	7	6.97	.17	.04	1.22	.33	3.72	.14	.05	<.08	.14
5663	8	7.65	.23	.04	.93	.39	1.90	.20	.24	.08	.08
5672	9	6.66	.61	.15	1.11	.62	6.10	.45	.10	<.08	.16
5661	10	7.49	.02	.02	.76	.65	2.76	<.03	<.05	<.08	.13
5664	11	7.88	.22	.05	.96	.38	1.90	.22	.26	<.08	.01
5662	12	7.60	.35	.04	.88	.36	1.98	.22	.24	.10	.08
5674	13	7.77	.21	.04	.85	.38	2.37	.22	.20	<.08	.01
5673	14	7.89	1.52	.07	.97	.39	2.29	.31	.95	.21	.08
5681	17	7.69	.20	.05	1.16	.22	2.98	.08	.14	<.08	.12

TABLE 2. Preliminary characterization of sediments from White Oak Creek Watershed. Grains of indeterminate classification not included in this compilation.

Sample	Site	Kd		percent gravel			fraction Fe-Mn coated grains*
		<sup>90</sup> Sr	<sup>137</sup> Cs	Chert	Carbonate	Shale	
		(ml/gm)					
Bethel Valley							
5426	8	14	700	21	30	37	11
5428	12	20	600	23	43	34	15
5434	10	22	131	75	4	21	73
5435	11	20	1100	13	47	40	18
5447	13	27	1600	49	23	28	46
Melton Branch							
5432	1	38	2200	40	0	60	27
5441	2	61	8500	4	2	94	44
5442	2	83	16000	1	2	97	43
5445	3	86	11000	1	2	97	31
5446	4	70	15000	0	0	100	36
5440	5	70	9900	3	30	67	38
5439	6	91	4600	0	0	100	37
5437	7	107	12000	1	0	99	73
5429	9	119	10300	3	0	97	87
5443	15	102	8200	1	2	97	37
5444	16	85	11000	0	0	100	54
5401	17	81	11000	0	2	98	3
5438	37	119	13000	0	0	100	75
5433	m*	37	5600	21	0	79	13

\* fraction of total grain surface having some Fe-Mn coating. Determined as described in text.

m\* 20 meters below confluence of Melton Branch with White Oak Creek.

Table 3. Continued.

Site	Mn	Mo	Ni	P	V	Zn
1	657	1.6	4.7	84	2.3	71
2	2300	1.6	4.8	130	2.0	90
3	1850	3.5	4.6	185	1.6	220
4	3000	.7	5.0	40	1.7	19
5	807	<2.3	4.5	123	3.2	14
6	2500	.7	4.9	34	2.2	4
7	4333	<.8	5.4	15	1.6	3
8	960	2.2	2.3	91	1.6	150
9	5400	7.3	420	19	1.2	10
10	2120	.4	2.8	25	3.4	20
11	350	2.3	3.3	74	2.0	170
12	920	2.2	2.6	100	1.7	150
13	1500	1.6	4.9	70	2.1	105
14						
15	3300	<.40	7.3	31	1.6	6
16	2400	4.7	7.3	340	2.3	340
17	2900	<.40	4.8	9	1.3	3
18						
19						
20	1600	<1.2	<2.4	<10	.9	4
21	920	<.40	.8	4	1.0	4
22	2600	<.42	6.6	14		4
23	1833	3.8	4.9	143	1.6	207
24	6067		4.1	51		16
25	3100		2.5	59		15
26	1633	<.40	4.1	31	1.9	11
27	2800		3.3	37		9
28	2433	4.0	5.3	157	1.1	217
29						
30						
31	705	1.8	5.0	90	1.5	101
32	1150	.47	3.6	12	1.9	12
33	1533	<.40	4.9	8	1.0	5
34	1234	.48	3.3	27	1.6	7
35	2400		2.7	13		28
36	1500		2.5	15		17

\* Pb was not listed because  
all values were non-detect-  
(Not extracted by procedure).

TABLE 3A. Extractable metals from gravels in White Oak Creek Watershed  
(in ppm).

Site	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg
1	497	39	1567	.31	6.5	16.3	2.1	1500	193
2	795	145	6300	<.05	11.5	11.2	1.4	2100	440
3	630	158	3800	<.06	11.2	14.2	2.8	2100	412
4	690	230	3000	<.05	11.0	6.1	1.7	3500	380
5	1930	63	20333	<.3	8.0	5.7	1.8	2567	2100
6	577	163	2600	<.05	14.	1.1	1.3	1533	410
7	653	160	3500	<.07	14.	0.7	0.9	1567	330
8	280	45	12000	.57	4.2	11.0	7.4	700	210
9	287	232	1573	<.1	6.8	0.8	1.5	1307	201
10	648	108	2490	.06	10.2	1.7	0.5	2775	180
11	240	20	18500	<.3	2.2	7.4	3.1	860	295
12	360	37	11000	.42	7.0	11.0	8.9	920	250
13	457	62	8000	.14	7.6	2.7	1.7	1500	203
14									
15	740	210	3000	<.05	17.0	2.0	1.8	3400	370
16	640	140	3500	<.1	12.0	11.0	15.0	3300	490
17	520	200	3000	<.05	17.0	.9	.5	1400	220
18									
19									
20	190	48	980	<.2	11.5	<1.2	<.6	495	44
21	275	40	2600	<.05	6.7	<.4	<.2	520	53
22	530	210	2450	<.05	17.5	<.4	.45	1450	310
23	477	163	2400	<.05	12.3	5.3	7.4	1867	363
24	697	257	2433	<.13	10.4	8.9	2.8	2733	380
25	313	148	6633	<.05	4.0	5.9	1.0	2533	330
26	427	170	2200	<.05	6.0	1.1	1.4	4433	430
27	400	177	3433	<.05	9.9	2.4	1.6	2067	343
28	430	153	3067	<.05	11.0	11.7	5.8	1533	373
29									
30									
31	325	52	2100	.18	6.2	12.0	5.0	1230	260
32	763	88	3300	<.05	17.2	.71	.60	1850	268
33	420	197	2200	<.05	11.0	<.40	.96	1467	413
34	574	129	5100	<.05	11.3	<.92	.44	1480	382
35	760	100	2500	<.05	14.0	<.40	5.1	1100	280